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CAPT. C. W. HUME, M.C., B.Sc.

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PROCEEDINGS AT THE MEETINGS OF THE PHYSICAL SOCIETY

SESSION 1933-34

Except where the contrary is stated the meetings were held at the Imperial College of Science and Technology, South Kensington.

October 6, 1933.

The PRESIDENT, Prof. A. O. RANKINE, O.B.E., D.Sc., F.Inst.P., in the Chair.

Meeting held in the Theatre of the Royal Institution, 21, Albemarle Street, W. 1.

Prof. R. W. Wood, Prof. F. Paschen and Prof. A. Sommerfeld were elected Honorary Fellows of the Society.

The President of the Optical Society of America was elected an ex-officio Fellow of the Society.

Arthur Elliott, Eric Arthur Howard French, and James Alfred Conway were elected to Fellowship of the Society.

The President announced that the Council had elected Derreck Henry Parnum to Student Membership of the Society.

The Thomas Young Oration was delivered by Dr HERBERT E. IVES of the Bell Telephone Laboratories, New York, who took as his subject "Thomas Young and the Simplification of the Artist's Palette."

October 20, 1933.

The PRESIDENT, Prof. A. O. RANKINE, O.B.E., D.Sc., F.Inst.P., in the Chair.

Rudolf Samuel was elected to Fellowship of the Society.

The President announced that the Council had elected Frank Holliday and R. C. Parker to Student Membership of the Society.

The following papers were read:

"The current-distribution round a short-wave frame aerial," by L. S. PALMER, M.Sc., Ph.D., D. TAYLOR, B.Sc., and ROY WITTY, B.Sc.

"The action of a tuned rectangular frame aerial when transmitting short waves," by L. S. PALMER, M.Sc., Ph.D., and D. TAYLOR, B.Sc.

"The rectifying peak voltmeter as a standard instrument," by A. T. STARR.

"Graphic statistics," by A. F. DUFTON, M.A., D.I.C.

November 3, 1933

The PRESIDENT, Prof. A. O. RANKINE, O.B.E., D.Sc., F.Inst.P., in the Chair.

P. V. Castell-Evans was elected to Fellowship of the Society.

The following papers were read:

"Note on the vibrating properties of metals at different temperatures," by MARY D. WALLER, B.Sc., F.Inst.P.

"The production of sounds from heated metals by contact with ice and other substances," by MARY D. WALLER, B.Sc., F.Inst.P.

"The band spectrum of barium oxide," by P. C. MAHANTI, M.Sc. (*In title only.*)

"The diurnal variation of the intensity of wireless waves reflected from the ionosphere," by F. W. G. WHITE.

"Some automatic records of wireless waves reflected from the ionosphere," by J. A. RATCLIFFE, M.A., and E. L. C. WHITE, B.A.

November 17, 1933.

The PRESIDENT, Prof. A. O. RANKINE, O.B.E., D.Sc., F.Inst.P., in the Chair.

Stanley James Davies and William George Penney were elected to Fellowship of the Society.

The presidential address, entitled "The Measurement of Magnetic Field Distortion," was delivered by Prof. A. O. RANKINE, O.B.E., D.Sc., F.Inst.P.

December 1, 1933.

The PRESIDENT, Prof. A. O. RANKINE, O.B.E., D.Sc., F.Inst.P., in the Chair.

George Herbert Leslie, Louis Melville Parr and Kenneth James Savage were elected to Fellowship of the Society.

The following papers were read:

"The image-distortion and other effects due to the glass-thickness in lens systems," by H. DENNIS TAYLOR, F.R.S.

"The tilted electrometer," by H. CARMICHAEL.

"The spectra of bromine V, VI and VII," by A. S. RAO and K. R. RAO. (*In title only.*)

"An automatic photo-electric photometer," by E. B. MOSS, B.Sc. (With demonstration.)

"A mechanical wave model illustrating acoustic and electrical phenomena," by G. D. WEST, D.Sc., F.Inst.P. (With demonstration.)

December 15, 1933.

The PRESIDENT, Prof. A. O. RANKINE, O.B.E., D.Sc., F.Inst.P., in the Chair.

W. H. Hoather, Eric Graham Knowles, Geoffrey David Pegler, and Percy Claude Vincent were elected to Fellowship of the Society.

The following papers were read:

"Crystal-structure and orientation in zinc-oxide films," by G. I. FINCH, M.B.E., F.Inst.P., and A. G. QUARRELL, Ph.D.

"Note on the behaviour of the Eötvös gravity balance in fluctuating gravitational fields," by A. O. RANKINE, O.B.E., D.Sc., F.Inst.P.

"The temperature variation of the orthobaric density of unassociated liquids," by ALLAN FERGUSON, M.A., D.Sc., F.Inst.P., and J. T. MILLER, B.Sc., A.Inst.P.

"The theory of the microscope, II," by L. C. MARTIN, D.Sc., A.R.C.S., D.I.C.

"The measurement of impact stresses in concrete," by G. GRIME, M.Sc.

"The preparation of heavy hydrogen," by P. HARTECK, Ph.D.

January 19, 1934.

The PRESIDENT, Prof. A. O. RANKINE, O.B.E., D.Sc., F.Inst.P., in the Chair.

The President announced that the Council had elected Alexander Jenkins, William Stanley Mabe, Stanley Ford Pearce and Arthur Harold Simons to Student Membership of the Society.

The following papers were read:

"The measurement of the inductance of iron-cored chokes carrying direct current," by E. O. WILLOUGHBY, B.E.E., B.A.

"A high-vacuum leak device," by G. A. WHIPPLE, B.A. (*In title only.*)

"On the use of charcoal in maintaining high vacua," by C. H. COLLIE, M.A., B.Sc.

"On some measurements of magnetic susceptibilities at high temperatures," by R. A. FEREDAY, Ph.D. (*In title only.*)

"The illumination-response characteristics of vacuum photoelectric cells of the Elster-Geitel type," by J. S. PRESTON, M.A., A.Inst.P., and L. H. McDERMOTT, A.R.C.Sc., B.Sc.

February 2, 1934.

The PRESIDENT, Prof. A. O. RANKINE, O.B.E., D.Sc., F.Inst.P., in the Chair.

Tikvah Alper, James Atchison, Georges-Albert Boutry, Gordon Frederick Lothian, Charles A. Mackay, Arthur George Quarrell, H. Dennis Taylor and Leslie Ronald George Treloar were elected to Fellowship of the Society.

The following presentations to the joint library were announced from the Chair as having been received since the last meeting: SWARBRICK, JOHN, *Easements of Light*, vol. I. SWARBRICK, JOHN and STEVENSON, A. C., *Easements of Light*, vol. II. Presented by the authors.

A demonstration on the subject of his paper, "The preparation of heavy hydrogen," was given by Dr P. HARTECK, of the Cavendish Laboratory, Cambridge.

The following papers were read:

"A new method of determining the magnetic susceptibilities of gases and vapours," by S. R. RAO, M.A., Ph.D., F.Inst.P., and G. SIVARAMAKRISHNAN, M.A. (*In title only.*)

"Magnetized ellipsoids and shells in a permeable medium," by L. R. WILBERFORCE, M.A.

"Hue-discrimination in normal colour-vision," by W. D. WRIGHT, A.R.C.S., D.I.C., Ph.D., and F. H. G. PITT, A.R.C.S., D.I.C., B.Sc.

"Intensity-distribution in molecular spectra: N_2 , second positive system," by N. R. TAWDE, B.A., M.Sc., Ph.D., A.Inst.P. (*In title only.*)

February 16, 1934.

The PRESIDENT, Prof. A. O. RANKINE, O.B.E., D.Sc., F.Inst.P., in the Chair.

Dady Barjoigi Boohariwalla, William Douglas Bradley and Lal C. Vemnan were elected to Fellowship of the Society.

The President announced that the Council had elected Robert Allen Nightingale to Student Membership of the Society.

Demonstration:

A demonstration of a magnetic torsion balance for the measurement of susceptibilities was given by the President.

The following papers were read:

"A note on integrals of products of experimentally determined magnitudes," by T. SMITH, M.A., F.Inst.P., F.R.S.

"Condensed tables for colour-computation," by T. SMITH, M.A., F.Inst.P., F.R.S.

"A relay memory for a thyratron counter," by C. E. WYNN-WILLIAMS, Ph.D.

"A note on the twisting-frequency in ethylene," by W. G. PENNEY, M.A., Ph.D.

"The instantaneous projection of thermionic valve characteristics," by F. C. CONNELLY, A.R.C.S., B.Sc.

March 2, 1934

The PRESIDENT, Prof. A. O. RANKINE, O.B.E., D.Sc., F.Inst.P., in the Chair.

Robert Albert Newing and D. O. Sproule were elected to Fellowship of the Society.

The following papers were read:

"A simple method of demonstrating the paramagnetism and diamagnetism of substances in magnetic fields of low intensity," by Prof. A. O. RANKINE, O.B.E., D.Sc., F.Inst.P. (With demonstration.)

"Anomalous changes in temperature due to thermionic emission in the filaments of valves," by A. M. FERASAH. (*In title only.*)

"Change of variables in Laplace's and other second-order differential equations," by T. SMITH, M.A., F.Inst.P., F.R.S.

"The Appleton-Hartree formula and dispersion curves for the propagation of electromagnetic waves through an ionized medium in the presence of an external magnetic field. Part 2: Curves with collisional friction," by MARY TAYLOR, M.A., Ph.D.

"An instrument for electrical prospecting by the inductive method," by J. MCGARVA BRUCKSHAW, M.Sc.

A demonstration of a high speed photographic camera was given by the staff of the Western Electric Co., Ltd.

March 16, 1934.

Annual general meeting.

The PRESIDENT, Prof. A. O. RANKINE, O.B.E., D.Sc., F.Inst.P., in the Chair.

The Minutes of the previous Annual General Meeting were read and accepted as correct.

The reports of the Council and Hon. Treasurer and the accounts were adopted.

The Officers and Council for 1934-35 and the Auditors were elected.

The eleventh Duddell Medal was presented to H. Dennis Taylor, F.R.S.

Vote of thanks were accorded to the retiring Officers and Council and to the Governors of the Imperial College of Science and Technology.

Ordinary meeting.

Charles John Birkett Clews, Henry Thomas Flint and Allen James Lewis were elected to Fellowship of the Society.

The following papers were read:

"The effective rotation temperature of the negative glow in nitrogen," by N. THOMPSON, B.Sc. (*In title only.*)

"The measurement of flame-temperatures in a petrol engine by the spectral line-reversal method," by S. S. WATTS, B.Sc., and B. J. LLOYD-EVANS, M.Sc., M.I.Mech.E.

"An apparatus for the determination of the dew point," by E. B. MOSS, B.Sc. (With demonstration.)

April 20, 1934.

The PRESIDENT, THE RIGHT HON. LORD RAYLEIGH, M.A., LL.D., Sc.D., F.Inst.P., F.R.S., in the Chair.

Hilda E. Carpenter was elected to Fellowship of the Society.

The President announced that the Council had elected Edward John Wenham to Student Membership of the Society.

The receipt of the following parts of Journals which have been presented to the Joint Library towards the completion of "runs" was announced from the Chair, and the thanks of the Society were accorded to the donors:

Proceedings of the Cambridge Philosophical Society, Vol. 14, Part 5, and *Transactions of the Cambridge Philosophical Society*, Vol. 20, Parts 9 and 10. *Presented by the Society.*

Journal of the Optical Society of America and Review of Scientific Instruments, Vol. 14, Parts 4 and 5, and Vol. 15, Part 2. *Presented by Mr T. Smith, F.Inst.P., F.R.S.*

Nova Acta of the Royal Society of Science, Upsala, Sweden. (Several parts.) *Presented by the Society.*

Proceedings of the Royal Society "A," Vol. 4 (1837-43) and part of Vol. 29 (1879). *Presented by Prof. A. F. C. Pollard, F.Inst.P.*

The following papers were read:

"Further experiments in illustration of the green flash at sunset," by the President, THE RIGHT HON. LORD RAYLEIGH, M.A., LL.D., Sc.D., F.Inst.P., F.R.S.

"An ultra-violet photoelectric spectrophotometer," by D. H. FOLLETT, M.A., A.Inst.P.

"The spectrum of trebly-ionized bromine," by A. S. RAO, M.A., D.Sc. and S. GOPALAKRISHNAMURTY, M.A. (*In title only.*)

"Note on the purity required for surface-tension measurements," by T. C. SUTTON, M.Sc., F.Inst.P., and H. L. HARDEN, B.Sc.

"Velocity modulation in television," by E. E. WRIGHT.

May 4, 1934.

The PRESIDENT, THE RIGHT HON. LORD RAYLEIGH, M.A., LL.D., Sc.D., F.Inst.P., F.R.S., in the Chair.

William Henry Dowland and Leslie V. K. Rein were elected to Fellowship of the Society.

The Nineteenth Guthrie Lecture was delivered by Prof. C. V. Boys, A.R.S.M., F.Imp.Coll., LL.D., F.Inst.P., F.R.S., who took as his subject "My recent progress in Gas Calorimetry."

May 18, 1934.

The PRESIDENT, THE RIGHT HON. LORD RAYLEIGH, M.A., LL.D., Sc.D., F.Inst.P., F.R.S., in the Chair.

The President announced that the Council had elected Harry Schecter to Student Membership of the Society.

The following papers were read:

"The longitudinal thermoelectric effect. I. Copper," by P. C. FENG, B.S., and Prof. W. BAND, M.Sc. (*In title only.*)

"A method for the measurement of the thermal diffusivity of poor conductors," by E. D. VAN REST, B.A., B.Sc.

"Measurement of the cell-space ratio in wood by a photoelectric method," by W. W. BARKAS, M.Sc.

"The determination of a parabolic formula to represent a series of observations," by J. H. AWBERY, B.A., B.Sc., F.Inst.P.

"The mid-course method of fitting a parabolic formula of any order to a set of observations," by T. SMITH, M.A., F.Inst.P., F.R.S.

"The linkage of CO and CO₂," by H. LESSHEIM and R. SAMUEL. (*In title only.*)

June 1, 1934.

The PRESIDENT, THE RIGHT HON. LORD RAYLEIGH, M.A., LL.D., Sc.D., F.Inst.P., F.R.S., in the Chair.

Frederick Allan Bannister, Harold Chevalier, Charles Richard Garrod Cosens, Gilbert King Johnson, Frank Llewellyn Jones and William Gregory Marley were elected to Fellowship of the Society.

The President announced that the Council had elected Iorwerth H. Thomas to Student Membership of the Society.

The following papers were read:

"The pressure of radiation. An historical statement," by Prof. G. F. HULL, Ph.D., S. E. GREEN, B.Sc., A.R.C.S., D.I.C., and MARY BELL.

"The estimation of small differences in X-ray wave-lengths by the powder method," by A. H. JAY, M.Sc., Ph.D.

"The action of alternating and moving magnetic fields upon particles of magnetic substances," by H. STAFFORD HATFIELD, Ph.D.

"Time scale and electron relay used with cathode-ray oscillograph for the investigation of switch-gear and circuit phenomena," by A. MORRIS CASSIE.

"Note on the hyperfine structure in the arc spectrum of xenon," by E. GWYNNE-JONES, Ph.D.

A demonstration of the theory of the green flash was given by Dr F. J. W. WHIPPLE, M.A., F.Inst.P.

June 15, 1934

The PRESIDENT, THE RIGHT HON. LORD RAYLEIGH, M.A., LL.D., Sc.D., F.Inst.P., F.R.S., in the Chair.

The following papers were read:

"The measurement of the electrical constants of soil by a Lecher-wire method at a wave-length of 1.5 m.," by R. L. SMITH-ROSE, D.Sc., Ph.D., A.M.I.E.E., and J. S. MCPETRIE, Ph.D., A.M.I.E.E.

"A determination of the electrical constants of the earth's surface at wave-lengths of 1.5 and 0.46 m.," by J. S. MCPETRIE, Ph.D., A.M.I.E.E.

"A spectrometer determination of the metrical thickness and dispersive power of a thin film," by O. DARBYSHIRE, M.Sc.

"The application of the theory of the transmitting echelon to the explanation of Talbot's and Powell's bands," by O. DARBYSHIRE, M.Sc.

"The thermal and electrical conductivity of metals and alloys: Part I, Iron from 0° to 800° C.," by R. W. POWELL, B.Sc.

MEETING AT THE ROYAL NAVAL COLLEGE, GREENWICH, JUNE 16TH, 1934

By the kind invitation of the President, ADMIRAL DOMVILLE and Prof. G. B. BRYAN a meeting of the Society was held at the Royal Naval College.

Experiments were shown in the Mechanics and Physical Laboratories. The Painted Hall and other historical features were open to inspection by members and their guests.

UNVEILING OF PLAQUE TO WILLIAM HYDE WOLLASTON

The unveiling of the plaque to William Hyde Wollaston on 14 Buckingham Street, W. 1, with the erection of which the Society had associated itself, was performed by Sir Frederick Gowland Hopkins, President of the Royal Society, on Wednesday, July 4, at 3.30 p.m. The proceedings took the form of a preliminary meeting held at the above-mentioned hour in the Royal National Orthopaedic Hospital, Great Portland Street; the meeting then adjourned to 14 Buckingham Street where the memorial was unveiled.

REPORT OF COUNCIL FOR THE YEAR ENDING FEBRUARY 28, 1934

MEETINGS

DURING the period under review 16 Ordinary Science Meetings were held at the Imperial College of Science and Technology. At these meetings 61 papers were presented and 5 demonstrations given.

By the kind invitation of the Western Electric Co., Ltd., a Science Meeting was held on March 3, 1933, in the lecture theatre of the Company at Bush House, when cinema films illustrating the use of an artificial larynx were shown and a demonstration given.

SPECIAL MEETINGS

On July 22, 1933, members and their friends visited Cambridge in response to the cordial invitation of Lord Rutherford and the Cambridge Instrument Co., Ltd. The morning was spent at the Company's works, where demonstrations were arranged of the various processes involved in the manufacture of scientific instruments. The research and development work in the laboratory was also on view. The party were the guests of the Company to lunch.

In the afternoon a meeting was held in the Cavendish Laboratory through the courtesy of Lord Rutherford. At this meeting a number of papers were read by Lord Rutherford and the workers at the Cavendish Laboratory; subsequently the party were entertained to tea and a number of demonstrations were given in the laboratories.

THOMAS YOUNG ORATION

On October 6, 1933, Dr Herbert E. Ives of New York delivered the Thomas Young Oration, his subject being "Thomas Young and the Simplification of the Artist's Palette".

The oration was delivered in the lecture theatre of the Royal Institution through the courtesy of Sir William Bragg and the Managers.

GUTHRIE LECTURE

The Eighteenth Guthrie Lecture was delivered on June 16, 1933, by Professor Manne Siegbahn of Upsala on "Studies in the Extreme Ultra-Violet and the Very Soft X-Ray Region".

INTERNATIONAL CONFERENCE

In the first week in October, 1934, an international conference on nuclear physics will be held in London and in Cambridge under the auspices of the Society. The conference will mark an epoch, as it will be the first of its kind to be held in England. It will be opened by Lord Rutherford.

The conference will meet in the same week as that of the London meeting of the International Union of Physics, and the conferences, especially on the social side, will be closely associated.

THE DUDELL MEDAL

The Tenth Duddell Medal was presented to Dr Wolfgang Gaede on June 16, 1933, for his work on vacuum pumps.

The Council has awarded the Eleventh Duddell Medal to Mr H. Dennis Taylor for his work on optical design.

ANNUAL REPORTS

Some time ago the Council sought the opinion of the Fellows of the Society on the desirability of initiating a series of annual reports on the progress of physical science. The unequivocal approval expressed by the Fellows, and the generous financial support which was forthcoming, have encouraged the Council to proceed with this project. In the autumn of 1934 a series of reports will be published in the form of a volume of some three to four hundred pages, which will be available to Fellows at a very moderate price.

EXHIBITION

The Twenty-Fourth Annual Exhibition was held on January 9, 10 and 11, 1934, at the Imperial College of Science and Technology by the courtesy of the Governing Body.

There were 81 exhibitors in the Trade Section and 29 in the Research and Experimental Section.

The following discourses were given: "The Evolution of the Galvanometer", by R. S. Whipple, M.I.E.E., F.Inst.P.; "The Instrumental Side of Colorimetry", by J. Guild, A.R.C.S., D.I.C., F.Inst.P.; "The History and Development of the Thermionic Valve", by Sir J. Ambrose Fleming, M.A., D.Sc., F.Inst.P., F.R.S.

REPRESENTATION ON OTHER BODIES

The Council of the Royal Society has increased the representation of the Physical Society on the British National Committee for Physics to three members. The three members now representing the Physical Society are Dr E. Griffiths, Mr T. Smith and Mr J. H. Awbery.

Mr J. H. Awbery, Dr A. Ferguson, Dr D. Owen and Professor G. F. J. Temple represent the Society on the Committee of Management of *Science Abstracts*, the number of representatives having been increased from two to four.

Professor E. V. Appleton and Dr A. B. Wood are the representatives of the Society on the National Committee for Radio-Telegraphy.

Dr D. Owen and Dr Ezer Griffiths represent the Society on the Board of the Institute of Physics.

OBITUARY

The Council records with deep regret the deaths of the following Fellows: Mr E. Barnes, Mr William Bennett, Mr G. J. Burns, Mr E. H. Coumbe, Rev. T. C. Fitzpatrick, Mr W. Gamble, Professor A. Hay, Sir Philip Magnus, Mr A. E. Mills, Mr F. J. Planel, Mr T. C. Porter, Mr J. B. Reiner, Mr R. C. Sclater, Mr L. R. Shorter, Professor W. C. Unwin (one of the Founder Fellows of the Society), Mr P. C. Young.

MEMBERSHIP ROLL

	Total Dec. 31, 1932	Changes during 1933	Total Dec. 31, 1933
<i>Honorary Fellows</i>	9	Elected 3	12
<i>Honorary Fellows (Optical Society)</i>	—	Transferred from Optical Society 8	8
<i>Ex-officio Fellows</i>	3	Elected 1	4
<i>Ordinary Fellows</i>	898	Elected 29	
		Transferred from Optical Society 36	
		Student transfers 2	
		<u>67</u>	
		Deceased 17	
		Resigned or lapsed 27	
		— <u>44</u>	
		Net increase 23	921
<i>Students</i>	54	Elected 12	
		Transferred to Fellow ... 2	
		Resigned or lapsed ... 4	
		— <u>6</u>	
		Net increase <u>6</u>	60
<i>Total Membership</i>	964	Net increase 41	1005

REPORT OF THE HONORARY TREASURER

THE accounts for the year ended December 31st, 1933 show an excess of income over expenditure of £512. 1s. 9d. This satisfactory balance is largely due to the increase in the sale of publications, especially of Dr Jevons' "Report on Band Spectra," the heavy cost of which was borne on last year's accounts. The estimated value of the Society's publications has been shown as a footnote on the Balance Sheet.

The announcement by the Council of the proposed publication of annual reports on the progress of physical science has resulted in several generous donations towards the cost. These are shown in a special account which amounts to £142. 2s. 0d.

The following investments were disposed of during the year to meet current liabilities:

£211 London County Consolidated $4\frac{1}{2}$ % Stock and £254. 2s. 9d. New South Wales 5 % Stock.

The Society's investments have been valued at market prices on December 31st, 1933, through the courtesy of the Manager of the Charing Cross Branch of the Westminster Bank.

(Signed) ROBERT S. WHIPPLE
Honorary Treasurer

February 23rd, 1934

BALANCE SHEET AS ON 31st DECEMBER, 1933

LIABILITIES				ASSETS			
	£	s.	d.	£	s.	d.	£
<i>Sundry Creditors</i>				1268	6	0	
<i>Life Compositions:</i>							
As on December 31, 1932	1718	0	0				
Less Transfer to Income and Expenditure Account of amounts paid by Fellows now deceased	96	0	0				
<i>Subscriptions paid in advance:</i>				1622	0	0	
Members	29	2	6				
Publications	158	16	11				
				187	19	5	3078 5 5
TRUST FUNDS							
<i>W. F. Stanley Trust Fund</i>				280	0	0	
<i>Duddell Memorial Trust Fund</i>				428	12	9	
<i>Optical Convention 1926, Trust Account</i>				81	18	3	
<i>"Special Reports on Physics" Account</i>				142	2	0	
							882 18 0
GENERAL FUND							
<i>Accumulated Fund:</i>							
As on December 31, 1932	2123	19	3				
Add increase in value of Investments	544	0	0				
Add Balance of Income and Expenditure Account	512	1	9				
				3180	1	0	
<i>A. W. Scott Bequest</i>				212	5	1	
							3392 6 1
							£7853 4 6

<i>Investments at Market Value on December 31, 1933:</i>							
£1500 Consolidated Stock 2½ %				1106	0	0	
£1000 War Loan 8½ % Inscribed "A" Account				1010	0	0	
£750 War Loan 8½ % Registered				758	0	0	
£650 Funding Loan 4 % 1960/80				726	0	0	
£500 India 8½ % Stock				428	0	0	
£400 Lancaster Corporation 3 % Redeemable Stock				364	0	0	
£390 London Midland and Scottish Railway 4 % Debenture Stock				415	0	0	
£1000 London Midland and Scottish Railway 4 % Preference Stock				700	0	0	
£500 London and North-Eastern Railway 4 % Debenture Stock				515	0	0	
£150 Southern Railway 5 % Debenture Stock				187	0	0	
£300 Southern Railway Preferred Ordinary Stock				192	0	0	
£442 Southern Railway Deferred Ordinary Stock				88	0	0	
£400 War Loan 8½ % Inscribed "B" Account				404	0	0	
							6893 0 0
<i>Dividends due from Investments</i>							84 10 11
<i>Inland Revenue—Income Tax claimed for 1933</i>							18 14 2
<i>Subscriptions due</i>							87 0 6
<i>Sundry Debtors</i>							112 5 11
<i>Cash at Bank</i>				255	5	8	
<i>Cash in Hand</i>				2	7	4	
							257 13 0

Stock of publications on 31st December, 1933. At
Honorary Treasurer's valuation . . . £1376 5 0

ROBERT S. WHIPPLE, *Honorary Treasurer.*

We have audited the above Balance Sheet and have obtained all the information and explanations we have required. We have verified the Bank Balances and the Investments. In our opinion such Balance Sheet is properly drawn up so as to exhibit a true and correct view of the state of the Society's affairs according to the best of our information and the explanations given to us and as shown by the books of the Society.

SPENCER HOUSE, SOUTH PLACE, E.C. 2
1st March, 1934.

KNOX, CROPPER & CO.,
Chartered Accountants.

LIFE COMPOSITION FUND ON DECEMBER 31st, 1933

59 Fellows paid £10	£	s.	d.
1 Fellow paid £15			
14 Fellows paid £21			
1 Fellow paid £30			
22 Fellows paid £81. 10s.			
	£	s.	d.
	590	0	0
	15	0	0
	294	0	0
	30	0	0
	693	0	0
	<u>£1022</u>	<u>0</u>	<u>0</u>

W. F. STANLEY TRUST FUND

Carried to Balance Sheet	£	s.	d.	£300 Southern Railway Preferred Ordinary Stock	£	s.	d.
	280	0	0	£442 Southern Railway Deferred Ordinary Stock	192	0	0
					88	0	0
	<u>£280</u>	<u>0</u>	<u>0</u>		<u>£280</u>	<u>0</u>	<u>0</u>

DUDELL MEMORIAL TRUST FUND

CAPITAL

Carried to Balance Sheet	£	s.	d.	£400 War Loan 3½ % Inscribed "B" Account	£	s.	d.
	404	0	0		404	0	0

REVENUE

Honorarium to Medallist	£	s.	d.	Balance on December 31st, 1932	£	s.	d.
Balance carried to Balance Sheet	20	0	0	Interest	30	12	9
	24	12	9		14	0	0
	<u>£44</u>	<u>12</u>	<u>9</u>		<u>£44</u>	<u>12</u>	<u>9</u>

OPTICAL CONVENTION, 1926, TRUST ACCOUNT

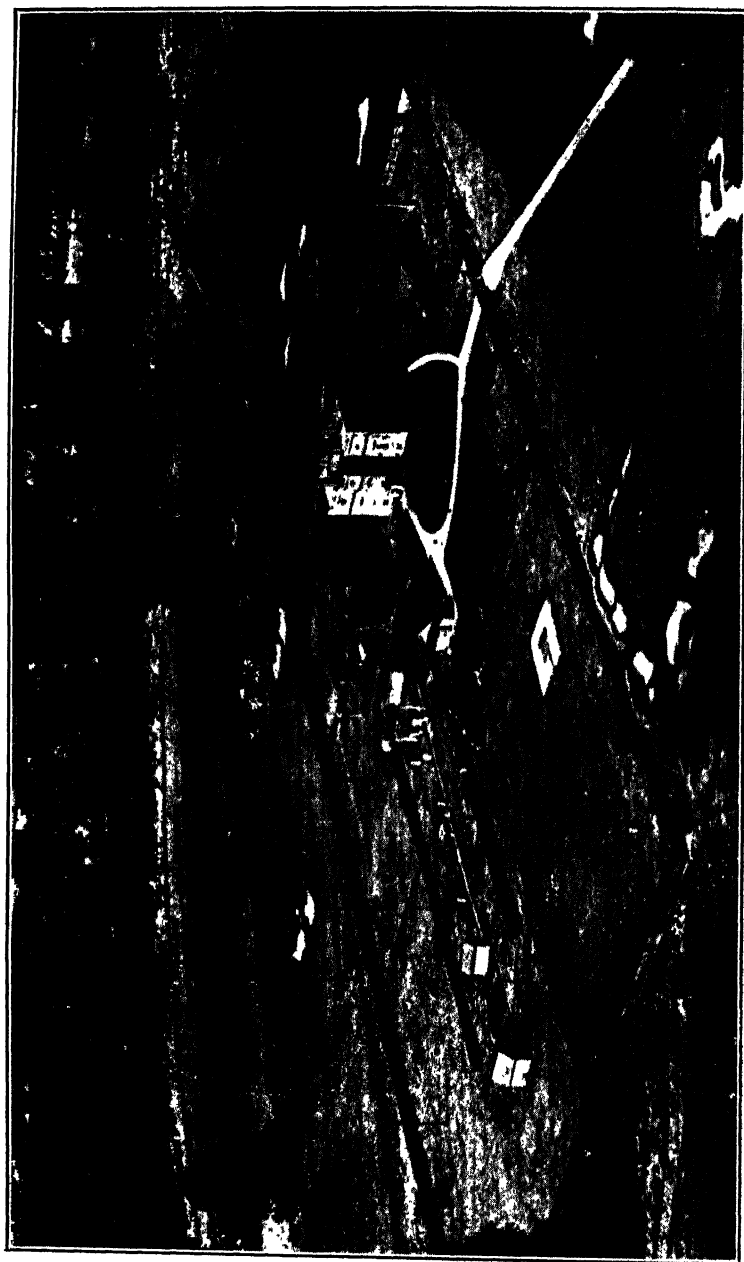
Balance carried to Balance Sheet	£	s.	d.	Balance on December 31st, 1932	£	s.	d.
	31	18	3	Sales of Publications	25	5	5
					6	12	10
	<u>£31</u>	<u>18</u>	<u>3</u>		<u>£31</u>	<u>18</u>	<u>3</u>

A. W. SCOTT BEQUEST

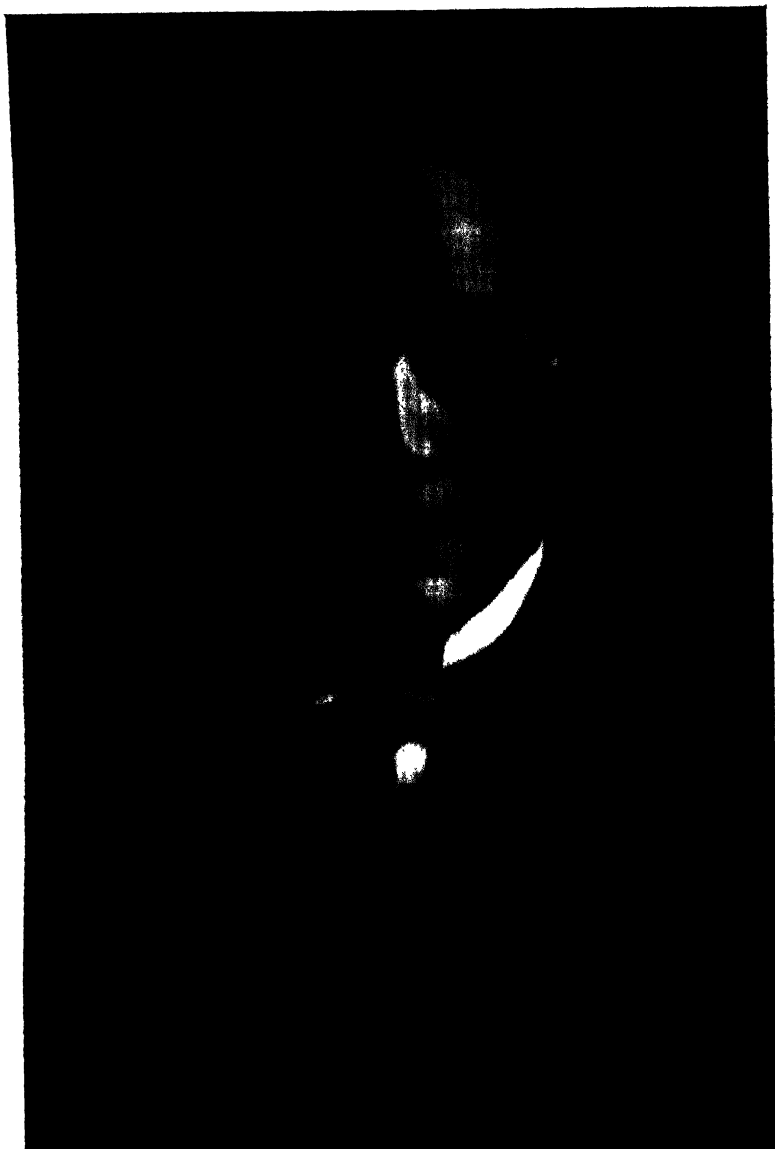
Expenses in connexion with Library	£	s.	d.	Balance on December 31st, 1932	£	s.	d.
Balance carried to Balance Sheet	37	14	11		250	0	0
	212	5	1				
	<u>£250</u>	<u>0</u>	<u>0</u>		<u>£250</u>	<u>0</u>	<u>0</u>

"SPECIAL REPORTS ON PHYSICS" ACCOUNT

Balance carried to Balance Sheet	£	s.	d.	Donations during 1933	£	s.	d.
	142	2	0		142	2	0



Kew Observatory from the air.



PROF. A. O. RANKINE, O.B.E., D.SC., F.INST.P.

President of the Physical Society, 1932-34

THE PROCEEDINGS ~~OF~~ ^{AGR.} THE PHYSICAL SOCIETY

VOL. 46, PART I

January I, 1934

No. 252

538.15

THE MEASUREMENT OF MAGNETIC FIELD DISTORTION

Presidential Address delivered on November 17, 1933 by

PROFESSOR A. O. RANKINE, O.B.E., D.Sc., F.INST.P.

ALTHOUGH it has not been the custom in recent years for Presidents to make particular reference in their addresses to the affairs of the Society, I feel that I must on this occasion depart from precedent to mention prominently one event of exceptional importance which has occurred during my period of office—I mean the union with the Optical Society. Of the wisdom of this step there can, I think, be no question. It was taken only after the Councils of the two Societies had assured themselves unmistakably of the mutual desire for amalgamation on the part of the members. The formal union took place in October 1932, and, at the end of March of the present year, the bulk of the members of the Optical Society had been received into the Physical Society—the modified name adopted by the Physical Society of London. Our Society now numbers more than a thousand members, and is, I am sure, much stronger and more active and useful than at any time in its previous history. As an officer continuously for fifteen years I have watched this growth from within with mixed feelings of satisfaction and pride, and to have the honour of being President at such a time is particularly gratifying to me. I believe our Society has before it a still greater future, in which I am still young enough to expect to share.

I have another reason for referring to the union with the Optical Society, namely, that I was President of that Society also. Luckily for me that Society ceased to have a separate existence in time to let me escape the duty of delivering a presidential address. Otherwise I should have had three addresses to prepare in the space of little more than a year, having presided also over Section A of the British Association in 1932. This escape left me with the half-formed intention to rectify the matter by choosing for my present address an optical subject. Indeed, I think I mentioned this privately to a number of Fellows. I have now to announce the abandonment of this project, and plead in excuse inability to find the necessary

time for preparation, optics being no longer the work upon which I am engaged. For several years I have been particularly interested in the relatively new subject of applied geophysics, and since 1931 I have been occupied in trying to establish in the Imperial College a small department for study and research in this subject. Accordingly I have chosen the easier path of addressing you now upon certain aspects of the work with which I am immediately concerned in the course of my ordinary duties.

I propose to discuss the possibility of improving the methods at present in use in magnetic surveying in relation to the determination of hidden geological structure. It is a subject definitely terrestrial, even trivial compared with the universe discussed by my brilliant predecessor. To be called upon to follow him weighs on me very heavily, and you must forgive me if the manner of my address merits the same comparison as the matter.

In the course of preparing lectures in the new department I have mentioned, I was brought intimately into touch with the torsion balance invented by Baron von Eötvös for measuring gravitational anomalies. Like all, I suppose, with similar experience, I became filled with surprise and admiration at the beauty of principle and practical efficiency of instruments of this type, and was able to present to the Society last year two papers on certain new aspects of theory and practice*. As a means of determining with precision the small variations of the earth's gravitational field the Eötvös torsion balance has become thoroughly established and is widely in use. I am indebted to Mr Lancaster Jones for the suggestion, which is at the root of what I have to say, that it might be possible to construct a *magnetic* torsion balance embodying the virtues of the gravity instrument, and thus enabling local magnetic variations to be measured in a similar manner. An examination of the literature revealed the fact that Eötvös himself had a similar idea—indeed that he actually constructed such a balance†. He does not appear, however, to have proceeded far with it, probably on account of certain practical difficulties. Later on I shall have to lay stress on these and admit that so far my experiments have not shown the way to eliminate them. It may even be that the object will not be attained until someone more capable turns his attention to the task. Yet for that very reason it seems worth while to formulate the great advantages which would attend a successful issue. Moreover, there does emerge from what has already been done the promise of a partial achievement not without interest in connection with the measurement of magnetic susceptibility.

There are, of course, already in use a number of portable magnetic variometers designed to indicate small local magnetic anomalies in particular regions of the earth's surface. Of these may be mentioned as typical the quartz-fibre horizontal-intensity variometer‡ used by Walker in his magnetic survey of Great Britain, the gravity-compensated horizontal and vertical magnetic variometers, due to Schmidt and now in very common use in geophysical surveying, and the recent adaptation to portability of F. E. Smith's current-compensated instrument for measuring the horizontal intensity. In all such instruments the small variations of magnetic force

* *Proc. Phys. Soc.* 44, 465–489 (1932).

† *Ann. der Phys.* 59, 373 (1896).

‡ This was indeed a torsion balance, but not depending on the principles here contemplated.

in passing from one station to a neighbouring one are made evident by balancing nearly the whole of the earth's magnetic control through the agency of a compensation subject to artificial adjustment. Thus in the Walker instrument the compensation is effected by applying torsion to the suspending quartz fibre; in the Schmidt variometers the magnetic couples are balanced by suitably disposed weights, and an opposing magnetic field procured by passing an electric current through a pair of coils arranged in the Helmholtz manner provides the necessary nearly complete compensation in the Smith apparatus. By means of these methods it has been possible to construct instruments capable of detecting under favourable conditions field-differences of rather less than 10^{-4} gauss* or 10γ at any rate in the horizontal intensity. But it is important to note that this degree of sensitivity is only attained as a result of nearly complete compensation of the main field.

A serious limitation is imposed by the effects of variations of temperature on the readings of these variometers. In geophysical practice wide changes of temperature have to be faced, and it is important to escape, if possible, from spurious effects arising in this way. Consider, by way of illustration, what is the effect of temperature upon a horizontal variometer of the Walker type. This instrument consists of a magnet suspended with its axis horizontal by means of a quartz fibre upon which there is imposed by means of a torsion head sufficient twist to hold the magnet approximately at right angles to the meridian. If the temperature changes, both the torsional coefficient of the fibre and the moment of the magnet are altered, and the equilibrium is disturbed to an extent proportional to the full value of the earth's horizontal field—a disturbance which may be much greater than the small genuine effects, the measurement of which is contemplated. In the Schmidt instruments temperature similarly affects the linear dimensions of the balancing arm of the compensating weight as well as the magnetic moment; and in the Smith apparatus there are variations of dimensions of the Helmholtz coils and of the e.m.f. of the standard cell used for current measurement. It is true that to some extent appropriate corrections can be applied, and that, indeed, in the Schmidt instruments, an ingenious temperature-compensating device has been incorporated. But it would clearly be advantageous to reduce the actual temperature effect to second-order proportions so that it would never be more than a small fraction of the small quantity measured. In the magnetic analogue of the Eötvös gravity balance this would be achieved.

A still more important advantage would accrue from the realization of a magnetic torsion balance corresponding to the Eötvös gravity instrument, namely, that it would differentiate between spatial and temporal variations of the earth's magnetic field if the latter were sufficiently wide-spread; it could deal with just such fluctuations as are experienced daily on the earth, and even magnetic storms. It would respond fully to the variations of field from point to point, but inappreciably to general time variations of the same order. Although the question does not really arise on the gravitational side, it is interesting to contemplate that if the earth's

* I am not sure whether it is still proper to call the field unit the *gauss*; I believe it should now be the *oersted*.

gravitational intensity were subject generally to small changes with time, the work initiated by Eötvös would not be handicapped. As it is, his instrument has not had the opportunity of displaying one of its chief virtues. In the magnetic case the position in this respect is, of course, different. It is a feature of the earth's magnetic field that it undergoes appreciable diurnal variations both in direction and magnitude, and occasionally there occur magnetic storms of still larger extent. As a result there are superimposed upon the magnetic effects of buried structure disturbances by no means negligible, which affect all ordinary magnetic variometers and mask the true anomalies sought. No artificial compensation is here possible, because the extent of the time variation is not known beforehand. The result is that it becomes necessary to apply corrections of rather uncertain amount by subsequent reference either to an established magnetic observatory or to an additional instrument set up at a fixed station for the purpose. This complication would vanish if we could use instead a magnetic torsion balance truly analogous to the gravity instrument, and at the same time the sensitivity of magnetic measurement would be greatly enhanced.

These important advantages of the Eötvös torsion balance—its very great sensitivity and its nearly complete independence of time variations of temperature and of field—are due to the peculiar nature of the compensation employed. The instrument is, in fact, self-compensating. In a spatially uniform field it adjusts itself automatically to a quiescent state, there being under these conditions no torsion in the suspending fibre. The line joining the point of support to the centre of gravity of the suspended beam becomes naturally a vertical axis, and the only forces which are operative in twisting the fibre are the small horizontal components of the gravitational attractions on masses displaced from the axis. Advantage is taken of the great sensitivity attainable in fibre suspension, and only the variation of the field—the main field itself being excluded—affects the orientation of the beam. The only limitation on sensitivity which gravity itself imposes is that it necessitates a fibre or wire strong enough to support the beam, and thus prevents indefinite reduction of the torsional coefficient.

I want to explain now how, at least theoretically, the principle of the gravity balance could be applied to an equivalent magnetic instrument. To do so may I remind you first of what the gravity balance actually measures directly. If it is simply a Cavendish balance, for example a suspended horizontal beam bearing at its two ends two equal masses, it measures those small distortions of the gravitational field represented by the quantities $\partial^2 U / \partial x^2 - \partial^2 U / \partial y^2$ and $\partial^2 U / \partial x \partial y$, where U is the gravitational potential and x and y are two arbitrarily chosen horizontal rectangular coordinates. If the beam system is modified, as in the Eötvös instrument, by displacing one of the masses vertically with respect to the other, e.g. by suspending it at a lower level from one end of the beam, two additional quantities are measured, $\partial^2 U / \partial x \partial z$ and $\partial^2 U / \partial y \partial z$, z being the vertical direction at the centre of gravity of the beam. Since $\partial U / \partial z$ is the local value of g , these two departures from uniformity of field are clearly $\partial g / \partial x$ and $\partial g / \partial y$, which we identify with the horizontal components of the gradient of gravity. We can, if we desire, express these in the form of a single

vector in the direction s making an angle ψ with x by the relations

$$\frac{\partial g}{\partial s} = \sqrt{\left\{ \left(\frac{\partial g}{\partial x} \right)^2 + \left(\frac{\partial g}{\partial y} \right)^2 \right\}} \quad \text{and} \quad \tan \psi = \frac{\partial g / \partial y}{\partial g / \partial x}.$$

For some purposes, as I have shown elsewhere*, it is indeed convenient to regard $\partial g / \partial s$ and ψ as primary magnitudes derived from the instrumental observations.

Now if we can copy the gravity balance so as to obtain a magnetic equivalent, corresponding magnetic quantities will be measured since U will now denote the magnetic potential instead of the gravitational. For example, the gravity-gradient will become the gradient in a horizontal direction of the vertical component of the local magnetic field. To impart to the balance these new functions it is necessary to substitute magnetic poles for gravitating masses, with due regard of course to the polar nature of magnetism—a property not displayed by gravitation. A consideration of the means of doing this shows that it would be preferable not to try to construct a single magnetic balance fully equivalent to the usual form of the Eötvös instrument, but to aim at making two separate instruments, one to measure the magnetic quantities $\partial^2 U / \partial x^2 - \partial^2 U / \partial y^2$ and $\partial^2 U / \partial x \partial y$, and the other to measure the magnitude and direction of the horizontal gradient of vertical magnetic intensity. A further reason for this division is that the second form seems to be more capable of practical realization, and may be conveniently considered by itself.

The magnetic analogue of the Cavendish balance would consist ideally of two equal magnetic poles of the same kind (say N) situated at or near the two ends of the horizontally suspended beam. Owing to the impossibility of isolating single poles whole magnets must be used, and the unwanted poles of the opposite sign must be so disposed as to produce relatively little turning effect. Two equal magnets, for example, with their south poles adjacent and near the axis of suspension, might be arranged with their axes directed precisely in opposite directions, and so form the beam. In a uniform field there would be no resultant turning moment in any azimuth; but particular kinds of spatial non-uniformity would give rise to a differential couple tending to twist the suspension, just as in the gravitational case. I have examined in some detail the magnitude of the small forces operative, in order to compare the possible sensitivity of the arrangement with that of the corresponding gravity balance. That is to say, account has been taken of the attainable pole-strengths in relation to the weights of the magnets possessing these poles, and the supporting strengths and torsional coefficients of available suspending fibres. I find that, with the very high values of remanent magnetism which can be possessed by cobalt steel, very great sensitivity can be anticipated. The relative position as regards magnetic and gravitational fields may be stated in this way. If we regard unit magnetic pole as equivalent to unit mass in the c.g.s. system, then, apart from the peculiar difficulties of construction or limitations of application to be mentioned later, the magnetic balance could be made several times more sensitive than the gravity balance. And, just as Eötvös found it convenient to define a small unit, 10^{-9} dyne/gm.cm. called the Eötvös unit, to express the small measured values of

* *Loc. cit.* and Presidential Address Section A, British Association, 1932.

such quantities as $\partial^2 U / \partial x^2$, we should need the corresponding magnetic unit 10^{-9} gauss/cm. for practice with a magnetic balance, if eventually forthcoming.

An interesting question arises in this connection. In field practice with the Eötvös gravity balance, corrections always have to be made on account of gravitational non-uniformity arising mainly from the rotation of the earth, and not attributable to local density-structure. One of these involves the quantity $\partial^2 U / \partial x^2 - \partial^2 U / \partial y^2$ which, except near the geographical poles, has an appreciable value. Physically this implies that the Cavendish beam system will tend to set perpendicular to the meridian of longitude. We may ask if there is any corresponding tendency in the magnetic case, in so far as we may regard the earth as a uniformly magnetized sphere. Calculation shows the answer to be in the negative, for both the quantities $\partial^2 U / \partial x^2 - \partial^2 U / \partial y^2$ and $\partial^2 U / \partial x \partial y$ prove to be zero under these assumptions; but I have to confess that so far I have been unable to picture physically why the astatic system described earlier should be in neutral equilibrium everywhere on the earth's surface. The result, however, is of significance. It means that the only deflections observable on a magnetic balance of this type would be those due to field-distortion arising from the local magnetic deposits which are the objects of search.

But I must proceed no further with this possibly too enthusiastic description without exposing the fly in the ointment. There is a very serious practical difficulty of construction which is quite likely to prove insuperable in respect of producing a field instrument for use at any arbitrarily chosen place. It arises from the fact that the earth's magnetic field is not everywhere nearly vertical. However useful the horizontal component may be to mariners, it is an unspeakable nuisance when we want to make really delicate magnetic measurements. Nor can the usefulness of the tangent galvanometer for instructional purposes reconcile me to H , whether properly specified in gauss or in oersteds. The existence in ordinary latitudes of this large horizontal magnetic force makes demands on our capacity for fine adjustment which seem likely to rob us of a large part of the sensitivity otherwise attainable, as well as making impracticable the use of magnet torsion balances following the normal procedure with gravity instruments. I can illustrate this by giving brief particulars of an instrument which I proposed at one time to construct. It comprised a metallic strip suspension 20 cm. long having a torsional coefficient of 0.007 dyne-cm. per radian. This had a breaking strength of 55 gm. wt. and was designed to support in the manner already indicated two cobalt-steel magnets each 5 cm. long and of mass 10 gm. Such magnets can have in practice moments of approximately 600 c.g.s. units, and, ideally, the completely astatic system contemplated would have displayed a magnetic sensitivity for indicating field-distortion of approximately 2 scale-divisions per 10^{-9} gauss/cm., as compared with $\frac{1}{10}$ scale-division per 10^{-9} dyne/gm.cm. in the original Eötvös gravity balance having the same optical magnification. In other words, for equivalent magnetic and gravitational field non-uniformity, the sensitivity would have been multiplied 20 times.

Only the difficulty of attaining the degree of astaticism to render the suspended system irresponsive to a uniform horizontal field prevents this precision being realized. But it is one so serious as to be, I fear, insuperable. In order to reduce the

effect of a uniform field of, say, 0.18 gauss to negligible proportions, i.e. to 1/10 scale-division, it would be necessary for the two magnets to have moments equal, and persisting in equality, to an accuracy of about 3 parts in a thousand million. Moreover, the alignment in opposite directions of the two axes must have a precision of less than one-thousandth of a second of arc. Of course, with smaller values of H the demand becomes less stringent. Indeed, in the immediate neighbourhood of the earth's magnetic poles the system could possibly be used. But these regions are limited—perhaps of radius a dozen metres—and we have no reason to suppose that geological deposits of great economic importance lie in these isolated parts. The whole argument, however, although disappointing in its results, is a remarkable illustration of the delicacy of the torsional suspensions which we have at our disposal.

I pass now to the consideration of another system which is not so unpromising—what may be called by analogy a magnetic gradiometer. In gravity surveying we have the gradiometer of Shaw and Lancaster Jones* in which the beam is designed so as to exclude what the Cavendish system measures, and to respond only to the gravity-gradient $\partial g/\partial s$. This instrument is sensitive enough to measure the gradient of gravity in a northerly (or southerly) direction, arising mainly from the rotation of the earth, which has a maximum value of about 8×10^{-9} dyne/gm.cm. in the latitudes 45° and is zero at the poles and the equator. The corresponding quantity in magnetism is $\partial V/\partial s$, V being the vertical component of the earth's magnetic field. Taking the earth as uniformly magnetized, calculation shows that $\partial V/\partial s$ varies from the maximum value of about 1.5×10^{-9} gauss/cm. at the magnetic equator to zero at the magnetic poles. The design of a magnetic gradiometer capable of measuring this gradient easily presents no difficulty save one, again due to the bugbear H , but not, I think, so great, which will be examined later. Indeed, the design in this case becomes particularly simple as compared with that required for gravity. Imagine a magnet hung with its axis nearly vertical from one end of a non-magnetic beam supported at the centre by the usual suspension and counterpoised with a non-magnetic mass attached to the other end. In a uniform magnetic field the resultant translational force on the magnet would be zero, since the poles are precisely equal and opposite in strength. It could only have a horizontal component in so far as H varied in a vertical direction, and it would thus be proportional to $\partial H/\partial z$ or $\partial^2 U/\partial s \partial z$, where s is the horizontal direction of maximum variation of H and z is vertical. The moment of this force would twist the central suspension to an extent depending upon the azimuth of the beam; thus the deflections would provide a measure of $\partial H/\partial z$. This differential coefficient can, of course, be identified with $\partial V/\partial s$, since both are equal to $\partial^2 U/\partial s \partial z$; accordingly the measurement of the horizontal gradient of the vertical magnetic intensity is implied.

One interesting point of difference between this system and the gravity analogue may be noted. In the latter, there being only one kind of mass, the two effective masses have to be arranged at different levels on *opposite* sides of the central suspension in order to isolate the differential effect to be measured. (This happens to

* This has recently been described fully in the *Journal of Scientific Instruments*, 9, 341 (1932).

be convenient also for counterpoising purposes.) The polar nature of magnetism requires for the corresponding effect that the two opposite poles should be on the *same* side of the suspension as indicated; luckily therefore no matching of different magnets is required as in the Cavendish form of instrument, and counterpoising can be effected by relatively non-magnetic materials. While on this point I may mention, in order to dispose of it, the question of possible confusion of magnetic and gravity effects. We cannot have magnets without inertia, and, in general, every magnetic torsion balance will be responsive also to gravity effects. Calculation shows, however, that, having regard to permanent magnetism in relation to mass in cobalt steel, it would be easy to secure that the gravity response shall be only a few per cent of the magnetic. Moreover, if necessary, advantage could be taken of the distinction between magnetism and mass by arranging such a distribution of the two in the beam as to render the system practically inert to gravitational anomalies.

If I give some details of a magnetic gradiometer I have designed and begun to construct, it may serve to illustrate further discussion on various points. The beam is 4 cm. long and has suspended from its ends by fibres of lengths not yet chosen a cobalt-steel magnet and a brass rod of equal weight. The magnet is a steel rod 5 inches long, $\frac{1}{8}$ in. in diameter and weighing 8 gm. Its determined magnetic moment is 570 c.g.s. units. The total weight is about 20 gm. and a phosphor-bronze strip suspension has been chosen of breaking strength 110 gm. wt. and torsional coefficient 0.024 dyne-cm. per radian. The calculated oscillation period of the system in the absence of magnetic effect is 330 seconds, which is of the same order as for gravity balances. Its sensitivity, which is determined by the ratio MI/τ , where M is the magnetic moment, l the length of the beam arm, and τ the torsional coefficient of the suspension, may be anticipated to be equivalent to that of the early Eötvös balance. That is, with an optical magnification (easily attainable) of 2000, one scale division would correspond to a magnetic gradient of 10^{-8} gauss/cm., which perhaps we may call by analogy 10 Eötvös magnetic units*. With this instrument the horizontal variation of V at the magnetic equator would be just detectable. Greater sensitivity is clearly at our disposal, but I have thought it wise not to push this to the limit thus early.

And now for the practical difficulty. It arises from the fact that the magnetic axis of the magnet may not be quite vertical. If so, there will survive a small but troublesome horizontal magnetic moment, tending to twist the suspending fibre which in turn will transmit a spurious torsion to the central suspension. I have given a great deal of attention to the ways and means of elimination of this effect, so far unsuccessfully. Having regard to the data previously given we must rule out, I think, the possibility of adjusting the magnetic axis to be truly enough vertical. Nor can I see how to attach the fibre with sufficient precision to the magnet to allow it to rotate about its slightly tilted axis without raising or lowering its centre of gravity. (If this were possible, of course, all torsion in the fibre would automatically vanish.) Alternatively, is it possible to find some form of suspension, fibre or otherwise, in which there is support against gravity with negligible torsional control? Fibre

* The Eötvös (gravity) unit is defined as 10^{-8} dyne/gm.cm. or 10^{-9} sec.²

materials are roughly equal in respect of the ratio between torsional coefficient and breaking stress. No great advantage is gained by choosing one rather than another; and for none is the ratio small enough for the present purpose. It is a problem that must have cropped up already many times in the design of physical instruments*, and the absence of solution means, I fear, that the present difficulty may also remain unsolved. It is not so much a question of loss of sensitivity, as in the Cavendish form of the balance. That could be reduced well below fifty per cent, and I shall show later how, apart from the application to magnetic surveying in the field, the proposed balance promises remarkable accuracy in laboratory measurements of susceptibility. But magnetic surveying would require in normal practice certain changes of azimuth of the beam to be effected merely by the rotation of the instrument as a whole. Even if, as might easily be arranged, the torsion in the suspension were approximately zero in one azimuth, it would not remain so for other necessary azimuths of the instrument, and the indirect effect of H would be to produce large spurious deflections which could not be conveniently observed in the optical system designed to disclose the small effects of field distortion. Very precise manipulation of the torsion head would be necessary—as, indeed Eötvös himself found—constituting a serious complication in a field instrument†. The other advantages of the completely astatic system also would not be fully realized.

I have thus to leave at present undetermined the question of the practicability of this second form of magnetic torsion balance for field use. But before doing so I wish to give an illustration of its powers of detection, if only its construction could be achieved. Perhaps this will serve also as a justification for the persistency with which

* As, for example, in the fluxmeter. But we are dealing here with a question of precision of a very different order.

† One of the chief reasons for the accuracy of the Eötvös torsion balance for field observations is that the torsion head is *not* adjusted in the field. The optical system is capable of measuring only small angles accurately—up to a maximum of less than 1 degree. Using the notation given later on, page 11, we can see the way in which H gives rise to comparatively large deflections masking the field-distortion effect: Suppose we turn the instrument into a new azimuth. This means that α , the azimuth of the torsion head, is changed to α_0 , and the geometrical relation

$$\alpha - \alpha_0 = (\theta - \theta_0) + (\phi - \phi_0) + (\epsilon - \epsilon_0)$$

holds. In a uniform field the equations of equilibrium are

$$\begin{aligned} \tau' \phi_0 &= \mu H \epsilon_0, & \tau' \phi &= \mu H \epsilon, \\ \tau \theta_0 &= \tau' \phi_0, & \tau \theta &= \tau' \phi, \end{aligned}$$

whence $\tau'(\phi - \phi_0) = \mu H(\epsilon - \epsilon_0)$ and $\tau(\theta - \theta_0) = \tau'(\phi - \phi_0)$.

Hence
$$\alpha - \alpha_0 = (\theta - \theta_0) (1 + \tau/\tau' + \tau/\mu H)$$

or
$$\theta - \theta_0 = \frac{\alpha - \alpha_0}{1 + \tau(\tau' + 1/\mu H)}.$$

This shows that $\theta - \theta_0$, the observed deflection, is not in general zero, as we should desire it to be under uniform field conditions. It is only if either τ' or μH is zero that $\theta = \theta_0$: in other words we must have one of three things—a negligibly small horizontal magnetic moment, a virtually zero horizontal field, or a practically torsionless subsidiary suspension. Without one of these conditions $\theta - \theta_0$ may be a large fraction of $\alpha - \alpha_0$, itself in practice amounting to π for one instrument-setting. For example, if μH is large and $\tau' = \tau$, then $\theta - \theta_0 = \frac{1}{2}(\alpha - \alpha_0)$, a large angle which cannot be measured in the field with sufficient accuracy to reveal precisely enough the small superimposed effects of slight non-uniformity of field.

mentally I have pursued the aim. Imagine a sphere of material of susceptibility K relative to its surroundings, buried at the magnetic equator with its centre at a depth below the surface equal to its diameter. Under the influence of the earth's field (here horizontal) it will become magnetized and produce at the earth's surface, vertically above, a small reduction ΔH of the earth's normal field, which proves on calculation to be given by

$$\Delta H = -0.17K.$$

It is independent of the radius and depth of the sphere because the effect of depth is just compensated by change of magnetic moment with altered size. We may choose ΔH so as to represent the present practical limit of sensitivity of horizontal variometers in common use. This is about 5γ , and the corresponding value of K in our example is approximately 3×10^{-4} c.g.s. units. Turn now to the magnetic gradiometer described. The value of $\partial V/\partial s$ which it measures directly above the sphere is given by $3\Delta H/h$, where h is the depth of the centre; or with the same value of ΔH

$$\partial V/\partial s = 1.5 \times 10^{-4}/h.$$

This equation makes evident an important distinction between the effects of buried magnetic deposits upon total change and upon gradient of magnetic intensity. The former does not vary with proportionate alterations of depth and linear dimensions of the deposit. On the other hand the gradient falls with increasing depth under the same conditions, as is shown by the appearance of h in the denominator. In the special case mentioned the magnetic force is inversely proportional to the cube of the depth; its gradient to the fourth power. This means that for the detection of large magnetic features at great depth the ordinary magnetic variometers, which measure ΔH or ΔV , will probably remain superior. At lesser depths, however, the advantage of the gradiometer becomes very marked. Thus, if our sphere is 15 metres in radius, and the depth of centre 30 metres,

$$\partial V/\partial s = 50 \times 10^{-9} \text{ gauss/cm.},$$

a value 50 times the anticipated sensitivity, under conditions in which ΔH would be only just measurable.

I pass now to consider the possible utility of the second magnetic torsion balance described, not as a field instrument but as a laboratory tool for accurate magnetic measurements. Here the main difficulty, I think, disappears. We accept the circumstance that the suspended magnet will in general have a small horizontal component of magnetic moment, causing it to tend to set with its axis in the plane of the meridian; also that in general this will give rise to torsion in the lower and central suspensions. This means that measurements must probably be made from a false zero. A diagram, figure 1, will illustrate the general angular relations; it relates to a plan of the apparatus. XX is the direction of H . AB represents the balance beam, the magnet being suspended at B and the counterpoise attached at A . The surviving horizontal component of the magnetic moment of the nearly vertical magnet is represented by cd , and ef indicates the azimuth of the torsion head above O . In the ideal position in which all the angles α , θ , ϕ and ϵ are zero no couple acts on any part of the system, and both fibres are free from torsion. It follows that in the displaced

equilibrium position represented, θ is the torsion on the central suspension and ϕ that on the fibre immediately supporting the magnet. From geometry

$$\alpha = \theta + \phi + \epsilon.$$

If the system is first in a uniform field and then subjected to any additional clockwise couple G , without alteration of the torsion head, θ , ϕ and ϵ , but not α , will change so that we have $(\theta - \theta_0) + (\phi - \phi_0) + (\epsilon - \epsilon_0) = 0$,

where θ_0 , ϕ_0 , ϵ_0 refer to the uniform field conditions (a) and θ , ϕ , ϵ to the modified conditions (b).

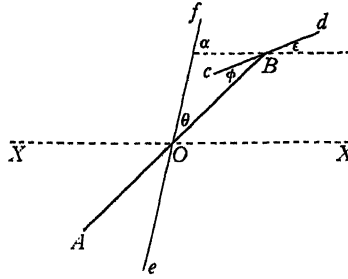


Figure 1

The equations of equilibrium for (a) are

$$\tau' \phi_0 = \mu H \epsilon_0^* \text{ for the suspended magnet,}$$

$$\tau \theta_0 = \tau' \phi_0 \text{ for the beam,}$$

where τ and τ' are the torsional coefficients of the central suspension and subsidiary fibre respectively, and μ is the horizontal magnetic moment, small in our case, but not necessarily so in the argument.

Under conditions (b) we have

$$\tau' \phi = \mu H \epsilon \text{ for the magnet,}$$

$$\tau \theta = \tau' \phi + G \text{ for the beam.}$$

On subtracting the corresponding equations we obtain

$$G = \tau (\theta - \theta_0) - \tau' (\phi - \phi_0)$$

and

$$\tau' (\phi - \phi_0) = \mu H (\epsilon - \epsilon_0).$$

Using the geometrical relation of angles first given, $\phi - \phi_0$ and $\epsilon - \epsilon_0$ may be eliminated, leaving G in terms of $\theta - \theta_0$, thus,

$$G = (\theta - \theta_0) \left\{ \tau + \frac{\tau'}{1 + \tau'/\mu H} \right\}.$$

The quantity which can be observed optically is $\theta - \theta_0$, although θ_0 itself is unknown. It is the change of deflection due to applying the additional couple G . The sensitivity of the arrangement is measured by $\theta - \theta_0/G$, and the effective torsional coefficient, which we desire to be small, is the rather awkward expression

$$\tau + \frac{1}{1/\tau' + 1/\mu H}.$$

* It appears in practice that ϵ will always be small, so that $\sin \epsilon = \epsilon$ nearly enough.

The positive addition to τ shows the diminished sensitivity arising from the existence of a horizontal field on the one hand, and the incomplete elimination of horizontal magnetic moment on the other. If μH were negligible the second term would vanish, and we should secure the maximum sensitivity represented by the reciprocal of τ . But even at the other extreme things are not so bad; for as H increases indefinitely the second term approaches τ' and the maximum effective torsional coefficient is $\tau + \tau'$. The magnet suspension can easily be assigned in practice a smaller torsional coefficient than the central suspension, for it has to support a smaller weight. Accordingly the sensitivity attainable is more than half the ideal.

A concrete illustration may be given to show how this still high sensitivity promises to facilitate accurate measurement. Consider the magnetic gradiometer already described, and let us assign to the fibre supporting the nearly vertical magnet a torsional coefficient equal to that of the main strip, namely, 0.024 dyne-cm. per radian. The strength of each of the poles of the magnet is about 50 c.g.s. units. Imagine a large (effectively infinite) slab of material placed with its vertical face parallel to the plane of the system so that the poles are distant d from the surface. The attraction on each pole arising from magnetic induction will be

$$f = \pi K m^2 / 2d^3,$$

where K is the susceptibility of the material of the slab, and m the pole-strength. With d equal to 1 cm.—a geometrically practicable condition—the total horizontal translational force on the magnet is $2f$ where

$$2f = \pi K m^2 / d^2 = 8 \times 10^3 K.$$

The couple G acting, the beam arm being 2 cm., is given by

$$G = 1.6 \times 10^4 K$$

and the observed deflection $\theta - \theta_0$ by

$$\theta - \theta_0 = G / (\tau + \tau') = 1.6 \times 10^4 K / 0.048 = 3.3 \times 10^8 K.$$

With K assigned even so low a value as that of air, namely 3.2×10^{-8} ,

$$\theta - \theta_0 = 0.01 \text{ radian,}$$

an angle easily made evident by ordinary optical means as a deflection of several centimetres. To realize approximately the proposed infinite slab of material we should require a suitable plane-faced vessel which could be evacuated at will. The entry and exit of the air or other gas could then be observed magnetically, and the possibility of somewhat precise measurement of susceptibility is apparent, under conditions in which the magnetizing fields are not large. The method would be a kind of inverted Curie balance, the magnet, instead of the test material, riding on the movable beam.

Finally I wish to add a few remarks on the question of the possible elimination of the effects of the earth's horizontal field. I do not think this would be practicable in a portable field instrument, on account of the size of the accessory apparatus which would apparently be necessary. But there is reason to believe that something could

be done in the laboratory to avoid the appreciable loss of sensitivity before mentioned, and to escape working from a false zero with its implications of temperature variability. Why should we allow the earth's field to exercise so much constraint? In my thoughts on this problem I have dreamt of a small laboratory which is devoid of magnetic force except from sources deliberately introduced. But, leaving that aside as too ambitious, we may consider how far a comparatively small space—large enough for a torsion balance of the size indicated—may be rendered magnetically free, at any rate in respect of horizontal force. With H small, as well as μ the horizontal magnetic moment, their product may be negligible in comparison with τ' , the torsional coefficient of the magnet suspension. This would imply that the sole control is exercised by the central suspension, which would attain a true zero of no torsion in any azimuth of the instrument as a whole, except when disturbed by the applied forces which we aim at measuring. The problem really amounts to this—Can we by artificial means cancel the earth's horizontal field to a sufficient extent?

I have made some calculations in this connection, based on available data for the materials and properties of magnets and suspensions. The assumption is also made that it would be possible to suspend the magnet with its axis so nearly vertical that the horizontal component of moment does not exceed $1/500$ of the total. This could be secured, I think, without too much difficulty. On this basis, if we could reduce the horizontal field to one-thousandth part of its natural value in London the surviving magnetic control would not be more than 1 per cent of that provided by the torsion of the central suspension. With more complete cancellation of the field its influence is, of course, correspondingly diminished. Under the conditions specified, also, there is no notable advantage in making the torsional coefficient τ' small, except in so far as suspension of the magnet by a flexible fibre rather than a more rigid attachment would probably facilitate the necessary adjustment of the magnetic axis to the vertical.

With the cancellation of H in view I have been making preliminary experiments with a pair of coaxial current-bearing coils adjusted to the proper azimuth. I believe that it will be possible to maintain over the current a control sufficiently precise to reduce the effective horizontal field for considerable periods to one-thousandth of the natural field, or even less. So far progress has been slow because of the variability of the magnetic field in the precincts of the Imperial College while London is electrically active. And even in the quiescent period, from 1 a.m. to 4 a.m. approximately, one is liable to be disturbed, as I have found, by magnetic storms. However, it is merely a matter of choice of suitable place and time to determine the practical possibilities of the arrangement, which will be described in due course.

I may perhaps refer to one aspect of the matter which is of some interest. The coils were designed to satisfy a condition of field-uniformity of 1 in 10^4 at 10 cm. from the centre of the pair arranged in the Helmholtz manner. This implied rather large dimensions—a diameter of about 2 metres. From motives of economy the formers were made of wood, and as it was considered easier in our workshop to make hexagons than circles of this size, the former shape was chosen. I am indebted to our carpenter, Mr Leech, for making these hexagonal formers accurate in all

respects to approximately two parts in a thousand, without the use of special tools. The choice of this shape necessitated the examination of the condition of separation appropriate to maximum field-uniformity near the centre of the pair. This led to a more general investigation in relation to plane regular polygons of any number of sides arranged coaxally with corresponding corners opposite one another. Several unexpected results appeared in the analysis. The first is the small variation of the distance of separation of the coils for maximum field-uniformity resulting from change of coil-shape. If we denote by b half this optimum distance, and by a the perpendicular from the centre of the polygon to any side, the ratio a/b has the value $\sqrt{3}$ for one extreme, namely, the polygon of 2 sides, and the value 2 at the other limit, the polygon with infinitely numerous sides. The first case, of course, corresponds to two pairs of very long wires, all parallel, and forming a rectangle in cross-section; while the latter is clearly realized in circular coils. For all other regular polygons a/b lies between $\sqrt{3}$ and 2, or a^2/b^2 lies between 3 and 4. I append a table, which may possibly be of use in other connections, giving a number of intermediate values.

Table 1

Number of sides of polygon	$\frac{a^2}{b^2}$	$\frac{a}{b}$
2	3.00000	1.73205
3	3.12153	1.77086
4	3.37284	1.83653
5	3.55561	1.88563
6	3.67454	1.91691
8	3.80725	1.95122
∞	4.00000	2.00000

With regard to the degree of field-uniformity at the appropriate coil-separation, the circular shape is best for a constant length of wire, as regards both the variation along the axis and that perpendicular to it. But the superiority in this respect is not great. The hexagon, for example, although inferior to the circle escribing it, is better than the inscribed circle. For the same perimeter the axial-field variation near the mid-point is only about 25 per cent greater for hexagons than for circles, and amounts to just less than 10^{-4} of the mid-point value at 10 cm. from the mid-point of the coils constructed, in which the perpendicular distance between opposite sides is 2 metres. A somewhat surprising result is with reference to the field variation in the medial plane perpendicular to the axis. It proves to be the same in the directions of the diagonals of the hexagons and of the perpendiculars between opposite sides. Moreover, its amount is exactly $\frac{2}{3}$ of the axial variation, just as Nagaoka* has shown it to be for circular coils arranged correspondingly. I hope to give a more complete description of this interesting field on a more appropriate occasion.

I must ask your indulgence for presenting to you a subject which remains so largely unfinished from the experimental point of view. On the theoretical side it has involved much work, and as I said at the beginning I have deliberately adopted the brain-saving device of addressing you upon the things to which spontaneously my thoughts have turned so often since I became your President.

* See F. E. Smith, *Phil. Trans. A*, 223, 187 (1923).

NOTE ADDED NOVEMBER 22, 1933

My statement on p. 3 that the Eötvös torsion balance has had no opportunity of displaying its virtue of immunity from the effects of temporal variations of gravity is incorrect. When I made it I had forgotten that there are in fact such fluctuations, the chief of which is a semi-diurnal one due to the moon. These are too small to be revealed by ordinary pendulum observations, but Loomis* measured the lunar effect for the first time in 1931, by comparing the rates of Shortt clocks and quartz oscillators. The complete absence of response of the Eötvös instruments in the extensive field practice of the last forty years proves in a most convincing manner that they exclude time variations of gravity and reveal space variations only. I propose later to communicate a short note giving some details of quantitative comparison between the small effective space changes and the large but ineffective time changes of the terrestrial gravitational field.

* *M.N.R.A.S.* 96, 569 (1931).

THOMAS YOUNG AND THE SIMPLIFICATION OF THE ARTIST'S PALETTE

The Thomas Young Oration delivered on October 6, 1933 by

HERBERT E. IVES

§ 1. INTRODUCTION

IN the year 1807 Thomas Young published in his *Lectures on Natural Philosophy* his observation that all the colours of the spectrum, and consequently all colours occurring in nature (since these are mixtures of spectrum colours) may be reproduced by mixtures of three—red, green and blue, or blue-violet as it is sometimes termed. Young represented his findings in the form of a colour triangle which is shown, carefully coloured by hand, in plate XXIX of Volume 1 of his *Lectures*. Much work in the way of scientific amplification and elucidation of Young's idea has been done since his time, notably by Maxwell and by Helmholtz, and the facts of three-colour mixture are the common property of scientific students of colour. In the field of technical application, three-colour photography and typographic printing have made extensive use of Young's discovery.

At the time Thomas Young published his three-colour theory, the great painters of the late eighteenth and early nineteenth centuries, Gainsborough, Reynolds, Romney, Stuart, Raeburn, and others, were painting their pictures with a set of pigments or "palette" which they had inherited from the old masters. The only theory involved in this palette was the primitive one of having a permanent and reliable colouring material approximating to each colour that the artist might want to reproduce. This primitive idea still dominates the artist's palette, for while the mixing of pigments is a common and unavoidable practice in the painting of pictures, the number of pigments in use is still very great. A. P. Laurie in his *Painters' Methods and Materials* lists some thirty odd reliable pigments for oil painting, and adds, "There are other pigments to be found in artists' colourmen's lists . . . but their name and number is legion." The average artist uses from twelve to twenty—Ingres used twenty-seven. Some artists, who have specialized in one line of work, are held up to admiration for the small number of colours with which they manage to get along—for instance Gilbert Stuart, who did his portraits with only seven colours. Usually, however, the work of artists who employ a limited palette is characterized by a preference for certain colours and colour combinations to which they are driven by the limitations of their chosen few paints. With such a vast array of pigments, greatly varying in their spectral absorption characteristics, it is a necessary consequence that there are many possible ways of achieving certain colours by mixture,

and also that some pigments will not mix to yield useful colours*. There can of course be no simple guiding theory covering the mixture of such a large array of pigments of all hues and varying degrees of saturation. Learning how to use his colours becomes a matter of rule-of-thumb experimentation and practice for each individual painter.

With the general scientific recognition of the great simplicity introduced into problems of colour-mixture by the observation of Thomas Young, it is a matter for surprise that no reflection of his work has appeared in the craft of the painter. There appear to be several reasons for this; the dominating one is probably that no professional scientist familiar with three-colour theory has been interested in painting. Conversely no competent artist has been sufficiently at home in optics to make a practical application of the three-colour principle. There exists among artists and teachers of art a belief, which is occasionally expressed very emphatically, that there is no connexion between the phenomena of light mixture and the practice of pigment mixture. Such attempts to use three-colour theory as are on record have failed for two reasons:

(1) Where it has been tried by artists there has not been a correct understanding of the transition from the *additive* mixture of red, green and blue light, to the *subtractive* or absorptive mixture which demands colours complementary to these, namely, a minus red (blue-green), a minus green (crimson or purple), and a minus blue (yellow). A long-perpetuated error has designated as pigment primaries red, yellow and blue. These, if pure, are three colours which could not be mixed to give by absorption the whole range of spectral hues. A number of artists have attempted three-colour painting, using approximations to pure red, yellow and blue, such as vermilion, chrome yellow and ultramarine, but with results which have been interpreted as discrediting the three-colour theory for use in painting. An explanation commonly given is that the pigments available are not sufficiently pure in colour. This, however, is an entirely erroneous idea, for it is only by their "impurity" that pigments mix to give other colours. Yellow and blue will give green only if they have overlapping regions of reflecting power, that is, if they are both impure. Reasonably pure red and blue pigments, having no overlapping spectral reflection regions, would simply give black, although the statement, carried over from additive colour-mixture, that red and blue make purple, is often found in artists' texts.

(2) As we shall see, even had anyone interested in the use of three pigments planned to use the proper colours, he would have been seriously handicapped until recently by the fact that reasonably correct colours have not long been available in satisfactory pigment form. He could not have attained success without the co-operation of the chemist in developing pigments which were unknown to the old masters or the contemporaries of Young.

* Thus the article of faith of many painters that "yellow and blue make green" is upheld by a mixture of lemon-yellow and Prussian blue, which have wide reflecting regions in the spectrum, leaving a band of residual reflection of green, but is contradicted by a mixture of ultramarine and chrome yellow, whose reflection bands scarcely overlap, so that the resultant green is quite dull.

§ 2. THREE-COLOUR PAINTING BY THE ADDITIVE METHOD

The most illuminating approach to the understanding of the principles of three-colour painting may be made by taking up first a theoretically interesting but impracticable method, which exactly parallels the mixture of colours by the additive mixture of three coloured lights. Let us reconsider, in somewhat more detail, the colour triangle of Young. Young drew this triangle as a straight-sided triangle lying in a plane, with red, green and blue at the vertices, and white (the mixture of red, green and blue) in the centre. Along the red-to-green side of the triangle lie orange, yellow and yellow-green, along the green-blue side the blue-greens, and along the red-blue side the various crimsons and purples. Mixtures of white with the colours on the edges of the triangle, or tints, lie at intermediate positions between the white centre and these colours. Later researches have shown that the true representation of the spectrum is not a triangle with straight sides, but one with slight curvature and a very blunt apex at the green corner. In terms of colour-mixture, this means that the mixtures of spectrum red, green and blue give colours which, while matching the rays of the spectrum in hue, are somewhat less saturated. The complete diagram is also not a triangle but a solid figure, of which Young's triangle is a cross-section.

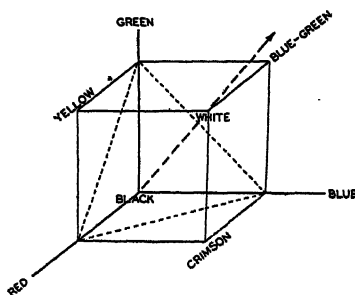


Figure 1. Trichromatic mixture phenomena represented by a colour cube.

This complete three-dimensional presentation of the phenomena of three-colour mixture is shown in perspective form in figure 1. Our figure is bounded by three straight-line Cartesian axes. The origin is the condition of no light, or black, the three axes represent red, green and blue light. Thus any line parallel to the red axis indicates addition of red light, any line parallel to the green axis addition of green light, and any line parallel to the blue axis addition of blue light. By proceeding along any one axis a chosen distance, then at right angles thereto, and then at right angles again for the same distance, one arrives at a point on the diagonal axis of the solid angle where the three colours are present in equal quantities, the black-white or grey line. The several possible paths made in this way define a cube, three of whose corners are red, green and blue; another three corners are the mixtures of red, green and blue two by two, and the remaining two corners are black and white. All possible colours, including tints and shades, are represented by points within this cube. The colour triangle of Young is the section of the cube, shown dotted, through the red, green and blue corners. Its centre is grey, and the spectrum lies

along its sides. If we imagine ourselves looking at this triangular section along the black-white axis of the cube, and imagine the cube as a hollow skeleton, we obtain the view shown in figure 2 *a* with the black origin at the centre. The primaries, indicated by arrows, to be used to make mixtures matching any colour can be picked by inspection, as those between which the colour in question lies. Interpreted in terms of the mixtures of three lights, red, green and blue, this cube tells us that we can project upon an unilluminated white (or black) screen, red, green and blue in various amounts and thus make all colours, with the reservations as to saturation already noted.

Let us now see how to apply these experimental facts to putting down our colours, not with light but with pigments. For this purpose we must start with the equivalent of the unilluminated screen, or in other words with a black surface. Our colours as we put them down must be red, green and blue, and should be opaque or capable in sufficient thickness of completely reflecting all the incident light lying within their range of spectral reflecting power. We cannot superpose these colours as we can superpose lights, for if transparent they will be mutually destructive, and if they were opaque only the top one would count. We must, therefore, place these down in

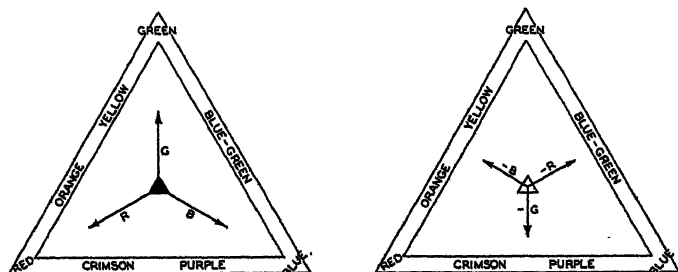


Figure 2. The section of the colour cube known as the colour triangle: (*a*) With the rear vertex of the cube exposed, to illustrate additive colour mixture; (*b*) With the front vertex of the cube displayed, to illustrate subtractive colour mixture.

juxtaposed small spots to be mixed by retinal fusion, and they should be chosen, for convenience, of such reflecting power that a group of spots of approximately equal area will together give the impression of grey or white. In order for the mixed colours to be as pure as possible the red, green and blue pigments should be of high purity of colour, that is they should reflect comparatively narrow spectral regions.

The technique of painting with these pigments consists in starting with a glossy black ground, such as photographers' ferro-type plate, and spotting on the three pigments in as small areas as is practicable, using large completely juxtaposed spots for the whites, and reducing the size of the spots, that is, leaving larger black areas between them and varying their relative proportions, to give all the mixed colours. Black, of course, remains where the ferro-type plate is untouched.

It is obvious that the technique of painting pictures by this method is very slow and difficult, and from that standpoint alone would have nothing to recommend it. There is, however, another unescapable defect of this type of picture, which is its inherent low luminosity or reflecting power. The brightest white which can be

obtained is that given by an area completely covered with juxtaposed pigment spots, whose individual reflecting power is extremely low and is lower the purer the pigments used. The reflecting power of such a white made with available pigments approximating to a monochromatic character will hardly exceed 10 per cent. A picture of this sort hung alongside ordinary pictures in which the whites have a reflecting power of 80 per cent or thereabouts, or in a room in which the whole range of brightness of coloured objects lies between the blacks and whites of 80 per cent reflecting power, appears hopelessly dull. If, however, one arranges to illuminate one of these three-colour pictures to approximately ten times the illumination of any of its surroundings, this handicap can be overcome*. For this purpose the picture should have a delimited spot of light such as can be produced by projecting the field of a lantern-slide projector upon it and surrounding the picture with an absolutely black area, for instance by mounting it in the centre of the open side of a box lined with black velvet. In order to achieve success in this scheme of illumination, the black ground must be of negligible reflecting power, which is approximately achieved by using a specular black surface such as the ferro-type plate, and the pigment spots should be laid on very flat so as to give no bright spots of specular reflection. The projection lantern should also, in order to avoid any specular reflection from the ferro-type plate, direct its light at a considerable angle to the surface of the picture from below or above. By utilizing this very special scheme of illumination one can carry through this method of painting in three colours, which closely exemplifies the additive three-colour mixture phenomena with coloured lights. It is obviously only of theoretical interest†. In passing we may recall that this kind of additive three-colour picture is illustrated by the autochrome process, in which the loss of light is one of the major defects.

§ 3. THREE-COLOUR PAINTING BY THE SUBTRACTIVE METHOD

The methods of painting which have come into practical use depend not upon the addition of colours to black, but upon the subtraction or absorption of colour from white. The final colours are due to residual reflecting power after the pigments are mixed together. An artist starts ordinarily from a white canvas and not from a black ferro-type plate. He starts also from a white which is of the same high reflecting power as the whites in the objects which will be in the same possible fields of view as his picture. It shall be our problem now to investigate how the three-colour principle may be applied to painting upon a white canvas by the process of absorbing light.

As a simple approach to this problem from the ground-work already set up, let us consider subtractive three-colour painting, starting not with the usual white canvas of high reflecting-power reflecting the whole spectrum, but with a white of

* This intensified illumination of course increases the surface reflections in the same ratio, and makes it difficult in practice to prevent a general greying over of the picture.

† The method used in this kind of painting was to a certain extent utilized by the "pointilist" school, who put down their colours in juxtaposed spots, and depended on retinal fusion or "vibration of colour" for mixture. The painters of this school, however, did not select red, green and blue as their colours, and used very unsaturated colours to get their greys and whites of sufficient luminosity.

the type considered in the last section, namely a surface uniformly covered with small juxtaposed areas of red, green and blue. This will appear grey alongside an ordinary white canvas, but, as has already been described, might for experimental purposes be raised to white by localized illumination. Let us now imagine that we provide ourselves with a pen charged with opaque black ink, such as India ink, and that we go over the red, green and blue spots and reduce them individually to spots of smaller and relatively different areas in different parts of the picture. Where we completely block them out we get black, where we block out the blue spots we get red plus green, that is yellow, where we block out the green spots we get purples, and where we block out the red spots we get blue-greens. If we are sufficiently patient and skilled, we can again produce a picture exhibiting all colours; here again, by a very impracticable process, which might be described as three-colour mezzotint. Referring to the colour cube of figure 1 our process consists in working back from the white vertex along directions parallel to the three axes, going in the reverse directions from those considered in the case of additive painting.

Let us consider now a variation of the procedure just described. Instead of using a finely pointed pen as our implement and confining ourselves to black ink, let us go one step nearer the technique of the artist and use brushes. Let us use three brushes each charged with a transparent absorbing paint such as water colour. One of these paints should have an absorption in the spectrum such that it obstructs or absorbs only the light reflected from the red spots, the second should absorb only the light from the green spots, and the third should absorb only the light from the blue spots. If now we take our three brushes and lay down on various parts of the stippled white surfaces various proportions of these three washes, we can with free brush stroke (thus getting away from the hampering microscopic spotting of the surface heretofore employed) proceed to paint a picture.

But an even simpler procedure is open to us. Instead of putting down the colours in three washes, let us mix them beforehand on a palette which is itself a red, green and blue stippled surface. We shall thus see upon the palette, as we mix our three washes, the colour which they will produce when laid upon the canvas. In this way we can mix and lay on (transparent) colours in practically the same manner as does the water-colour artist who works in aquarelle. Our resultant picture is subject to the same limitations as to brightness and necessary conditions of illumination as the additive one we have previously produced.

Before we go on to the problem of painting on a truly white canvas, there is one more approximation we could make to the technique of the painter in oil colours. A great working advantage of oil paints is that one is emancipated from dependence upon the white canvas for whites or admixtures of whites. The artist can at any time restore the canvas, as it were, by mixing white pigment with his colours and painting over earlier work at any stage. We could parallel the regular oil-painting technique with the subtractive process as thus far described by providing ourselves with a white pigment which reflected only three narrow spectral regions just as does the special canvas we have used. This point is brought up merely to aid in introducing the complete technique of three-colour painting in oil to be discussed in detail.

Let us consider the appearance and characteristics of the three colours and the white which we have just imagined ourselves using to build up a picture by the subtractive or absorptive process. The white is, of course, what would ordinarily be described as a dark grey. As we apply each one of the colours alone over the grey, we note that their colours are complementary in hue to the additive primaries red, green and blue. The colour which absorbs the red leaves a mixture of blue and green, that is a blue-green. The colour which absorbs the green leaves a mixture of red and blue, which is a crimson or purple; the colour which absorbs the blue is a mixture of red and green, or yellow. When we use these colours in pairs we obtain the primaries for mixtures of light, that is red, green and blue. When we use all three, we obtain black.

By way of review and crystallization of the ideas which have just been developed let us refer to figure 3. In diagram *a* we have represented the additive mixture of red, green and blue, building up to a trichromatic white, of low reflecting power. In diagram *b* we have represented the subtractive method as just described, starting with a trichromatic white and arriving at black by absorption.

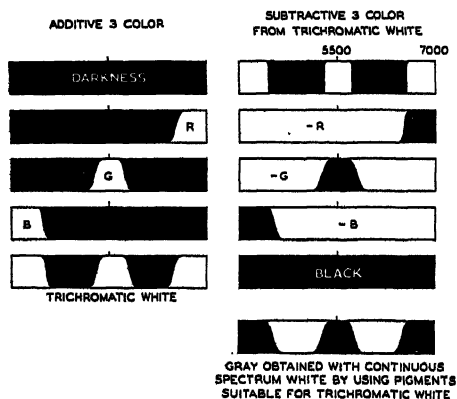


Figure 3. Additive and subtractive three-colour mixture illustrated.

Now the colours which we have used in this subtractive method are unspecified as to the extent of their spectral absorptions. They must merely absorb one of the additive primaries and nothing of the other two, but as to their behaviour in the spaces in the spectrum between the tri-colour white it has not been necessary to make any restrictions, for these spaces are non-reflecting and contribute nothing to the final result. Let us now go over to the practical case of the use of a truly white canvas, with an ordinary white opaque pigment such as zinc oxide for restoring the canvas or for admixture with the coloured pigments to reduce their saturation. These whites, unlike those trichromatic whites considered above, reflect the whole of the visible spectrum. A question fundamental to our problem is this: starting with a continuous-spectrum white, can we postulate three absorbing media which, as their mixing proportions are varied, will yield the same range of colours as absorptions applied over the trichromatic white? Specifically can we imagine three pigments

which (1) together absorb the whole spectrum to give black; (2) in pairs give satisfactorily pure red, green and blue; and (3) singly give yellow, crimson and blue-green matching the mixtures of pure red, green and blue in pairs?

Taking up these specific requirements in turn we note first, by reference to the lowest sketch of figure 3 *b*, that the localized absorptions which sufficed with the trichromatic white will not together cover the spectrum and give black. *For this purpose the absorption bands of the three pigments must meet or overlap.* If they merely meet, it will be possible to produce a black but the three primaries obtained by using them in pairs will consist of broad sections of the spectrum, instead of the practically monochromatic red, green and blue we want. In order to secure primaries of high purity (our second requirement) it is therefore necessary to have absorptions which overlap. At the same time the non-overlapping portions of any two must be free from absorption so that the residual colours shall be as bright as possible. Such absorptions are shown in the colour triangle in figure 4. As to the third requirement



Figure 4. The absorption regions of the three subtractive primaries represented in the colour triangle.

above listed we find the desired property to be guaranteed by the colour triangle construction. Upon plotting our three absorptions meeting the first two requirements upon the colour triangle, as shown in figure 4, we see at once that the minus red, minus green and minus blue constitute the flat sides of the triangle, that is, the extended portions of the spectrum which match in hue the mixtures of their two ends. In other words the additional light admitted from the continuous-spectrum white as the three absorptions are varied in extent or intensity is of a hue which is always of the kind we desire to produce by mixtures in the case of the trichromatic white.

We have thus far considered merely the question of hue, finding that we can handle it satisfactorily with a set of minus colours. In addition there are the factors of luminosity and saturation to be studied. In the cases we have considered where trichromatic whites were used, luminosity and saturation were automatically taken care of because the same elements entered into the whites and the colours. Can we, with the absorptions rendered necessary by the basic continuous-spectrum white, make mixtures which preserve luminous values, as do additive or subtractive three-colour mixtures using a trichromatic white? The answer is in general in the negative. The fact we must recognize is that whenever, by the subtractive method here considered, a subjective colour match is made, different in spectral composition from the sample, different portions of the spectral luminosity curve are affected so that a simultaneous hue and luminosity match is prevented.

This behaviour of subtractive mixtures of the type we are considering is made evident by applying the information contained in the three trichromatic excitation

curves and the luminosity curve of the spectrum, figure 5. As a typical illustration consider a lemon yellow, owing its colour to a narrow but intense absorption in the extreme blue of the spectrum, as shown in the dotted areas of the excitation (A) and luminosity (B) curves of figure 5 and in the spectrophotometric plot (C). Let us now endeavour to match this by using, with white, absorption bands of the kinds shown in figure 4. Let us assume that, upon admixture with white, these absorption bands remain of constant width, merely changing in intensity. Our process of making a match in hue would then consist in first mixing a certain amount of minus blue (yellow) with the white as shown by the cross-hatched area to the left in figure 5 C. This absorption would extend well into the green excitation curve of figure 5 A,

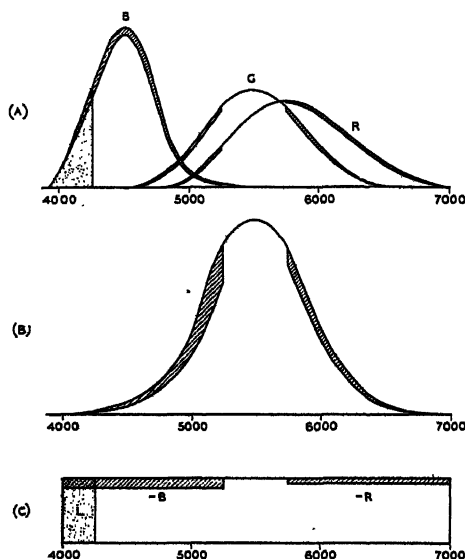


Figure 5. Luminosity and saturation problems in subtractive three-colour mixture illustrated.

making the resultant colour too orange. To offset this the red excitation curve will have to be reduced by the admixture of some minus red, as shown by the cross-hatched areas to the right. By this means the balance of red, green and blue excitation curves is restored, that is, a hue match is obtained. However, on reference to figure 5 B, where the same absorptions are represented in luminous values, it is at once evident that we have obtained our hue-match by encroaching upon the central more luminous portions of the spectrum; our mixed colour is too dark.

From this illustration, which is more or less representative, we see that subtractive mixtures obtained in this way from a continuous spectrum white, running darker than natural colours obtained from narrow intense absorptions, will drive us to paint in a lower key than a palette consisting of an extended range of pigments might permit; or, as an alternative, to raise the luminosity by greater admixture of white, thereby reducing the saturation. If the latter is done, then to the loss of

saturation already noted as inherent in trichromatic mixture is to be added a loss of saturation due to the use of a continuous-spectrum white*.

The situation is not, however, as serious as it might appear from the above illustration. Actual pigment absorption bands do not decrease merely in intensity on dilution with white. They simultaneously become narrower, in the manner shown in figure 6 where three idealized pigments are postulated, conforming in their concentrated form to the requirements given in figure 4, and behaving on dilution in a manner which is typical of pigments which might reasonably be expected to be found or produced. With such absorptions matches with colours due to narrow absorption bands will be made to a considerable degree by an actual narrowing of absorption bands in the mixtures, and so the need for lowering the key will largely be eliminated. In addition to this alleviating fact is the very general phenomenon

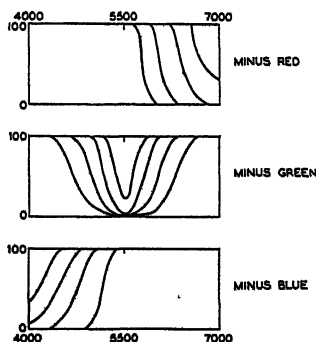


Figure 6. Ideal reflecting characteristics for three-colour pigments as diluted with white.

that all colours encountered in naturalistic painting are themselves quite unsaturated, in other words, the kinds of colours which give trouble in three-colour subtractive mixture are of rare occurrence. Also, if we are comparing a three-colour palette with the existing painter's palette, we must not forget that very few of the reliable pigments now used exhibit narrow, sharply defined, or intense absorption bands. In fact, the limitations which have been conscientiously pointed out in the three-colour palette are present also in large degree in the ordinary artist's palette. We have therefore a reasonable expectation that a simple three-colour palette of absorbing media of the kind specified by figures 4 and 6 will make satisfactory mixed colours for all ordinary painting. If, on the other hand, it proves deficient in practice, we are in an excellent position to know how to modify it in a scientific manner to meet all requirements.

We are now ready to consider the experimental test of the theory. This test consists in obtaining or producing three pigments approximating in satisfactory degree to the characteristics depicted in figure 6, and trying practical painting

* With such absorbing media as are actually available other faults, such as spreading of the absorption over spectral regions which should be clear, incomplete absorption at the centre of the absorption band, lack of proper transparency, etc. are probably much more serious.

experiments with them. Mixed together in varying proportions the three pigments should satisfactorily reproduce the hues of the spectrum. From these spectral matches mixtures with white will then give all the tints. Further mixture with black (combination of all three pigments) will then give all shades.

§ 4. PRACTICAL TEST

Although the general scheme for the simplification of the pigments used in painting, which has just been described, is applicable to any form, such as water colour or fresco, I have confined my attention to oil painting as the most powerful and flexible method. This study naturally divides itself into two stages; first is the stage of finding or producing a set of three pigments which shall have the proper character of absorption, in order to prove the correctness and advantages of the idea. The second stage, granted the success of the first, is to obtain or produce pigments of the required character which shall have other characteristics, such as fastness to light and freedom from chemical interaction, which are indispensable if the pictures painted are to have satisfactory permanence.

In regard to colours which shall be capable of proving the theory, certain characteristics other than those specified by the character of the absorption are desirable. It is, for instance, quite necessary, if pure brilliant colours are to be produced in the final picture, that the pigments give as little admixed white light by surface reflection as possible. This means that the pigments should have very intense colouring power and should have a considerable degree of transparency. They must, however, because of the nature of oil painting, be sufficiently opaque in concentrated form to ensure that under-painting shall be completely obscured.

On a preliminary survey, the colours called for appeared to be quite far from any available among the common artists' pigments. Accordingly an extended search was made, largely by spectro-photometric analysis*, in the field of organic dyestuffs. As a result of this search I have been able to select a set of three colours of a high degree of permanence which approximate fairly satisfactorily the ideals above postulated. These are, for the blue-green a tungstic acid lake of the basic dye Glacier blue; for the crimson a tungstic acid lake of Rhodamine 6-G; for the yellow the pigment known as Hansa yellow 5-G. The reflection spectra of these, with various dilutions with white, are shown in figures 7, 8 and 9. It will be seen that the yellow is a very satisfactory approximation to the ideal postulated; the crimson is fairly good, its defect being too low a reflecting power at the ends of the spectrum, particularly in the blue. The weakest member of this series is the blue-green; it is of the proper hue, but reflects some deep red, is of comparatively low reflecting power in the blue and violet of the spectrum, and exhibits, in general, too narrow a band of reflection; it approximates to a spectral blue-green rather than a minus

* I am indebted to Prof. A. C. Hardy of the Massachusetts Institute of Technology for making the very large number of measurements by means of his photoelectric recording spectro-photometer. The curves shown are all in terms of magnesium oxide as a standard white.

red*. Nevertheless, in spite of their obvious deviation from the ideal, this set of colours proves to be remarkably successful in copying most of the commercial artists' pigments and is notably better than any of these latter for producing certain colours such as purples. Because of the low reflecting power of the blue-green lake

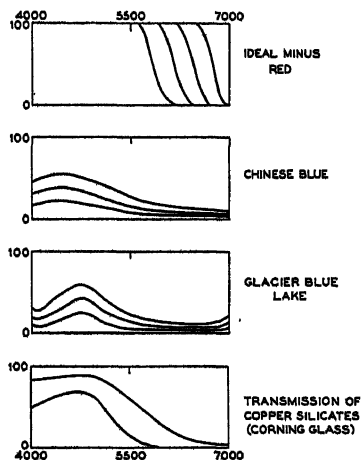


Figure 7. Ideal and available minus reds.

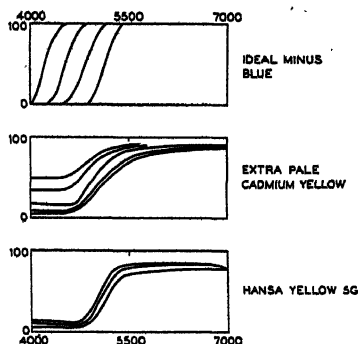


Figure 9. Ideal and available minus blues.

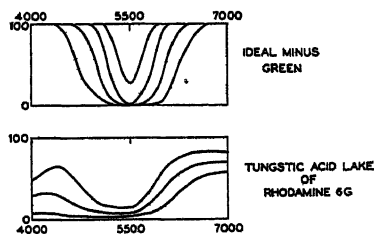


Figure 8. Ideal and available minus greens.

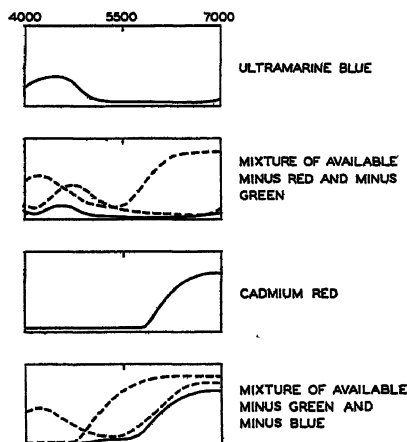


Figure 10. Illustrative mixtures obtained with the experimental three-colour palette.

* It is of interest to note that the colouring-materials commonly used for yellow are all true minus blues—the whole spectrum diminished by absorption in the blue—and are hence of high luminous value. On the other hand, all pigment blue-greens, with the single exception of cerulean blue (cobalt-tin-magnesium oxide) approximate toward monochromatic blue-green, and are hence of low reflecting power as well as being unsuitable for a subtractive three-colour pigment. A recurring difficulty in attempting to secure minus-red pigments in these experiments has been that all practical pigment makers instinctively turn to some mixture of blue and yellow-green, such as cobalt blue and chromium oxide, and have trouble in grasping the idea that the same hue should be obtainable by mere absorption in the red. The parallel situation in the case of yellows would be, if these were habitually produced by mixtures of orange and Prussian blue, best described as dirty browns.

in the blue, brilliant blues such as are given by ultramarine are not well rendered. This, however, is nothing to the discredit of the underlying theory as the reason is perfectly evident from the spectro-photometric curves. Figure 10, which gives spectro-photometric curves of representative mixtures, illustrates the unsatisfactory character of the blues, as just noted, and the excellent spectroscopic match with a common artist's pigment red*. With this set of colours it is possible to paint a representation of the spectrum of great fidelity, affording a convincing testimony to the validity of the theory. This set of pigments suffices to prove the soundness of the three-colour method.

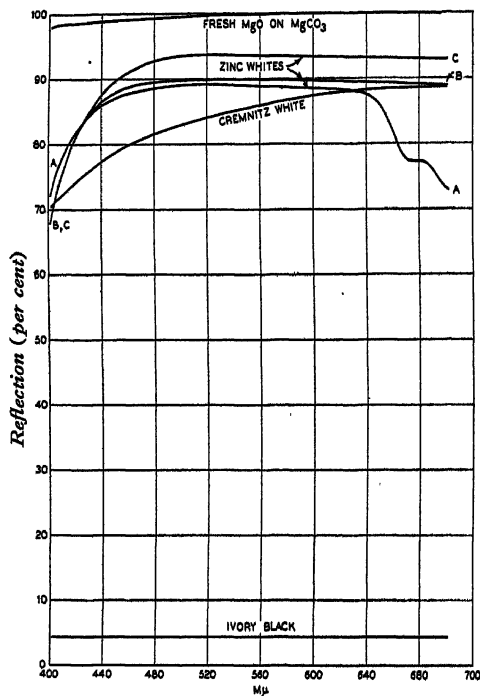


Figure 11. Reflecting power of various white pigments ground in oil.

From the standpoint of permanence, which is always questioned at once by the serious artist, the three organic pigments above listed are extraordinarily good compared with anything in this class available a decade ago. Pictures painted with them may be expected, on the basis of forced-fading tests, to last unchanged under ordinary gallery lighting for a lifetime. However, in addition to the closer approxi-

* An additional reason for the relatively poor rendering of blues is the fact that the medium (linseed oil) is definitely yellow, and, as is well known, becomes yellower with age. A decided drop in reflecting power, amounting to about 25 per cent in the extreme blue, is shown by all the spectro-photometric curves without exception. This is illustrated by the curves for several samples of zinc white, shown against magnesium oxide as standard in figure 11. The satisfactory realization of the three-colour method calls, even more than ordinary oil painting, for a colourless non-yellowing medium. Experiments which have been described on the use of silicon ester, by King, *J. Oil and Colour Chemists Assn.* (v), 13, 28 (1930), are of great interest in this connexion.

mation to the specified spectral characteristics which is still to be attained, an even higher degree of permanence is desirable. In searching for satisfactory pigments of greater permanence I have been able to make substitutes for the yellow and the blue-green from available artists' colours which are not only more permanent but are on the whole somewhat better in performance. For the yellow I find that "extra pale cadmium yellow" (cadmium sulphide prepared at high temperature) is an exceedingly close match to the Hansa yellow 5-G both visually and spectro-photometrically. Its absorption, figure 9, extends slightly further into the green, thus contributing better toward filling the space between blue and green, while when diluted with white it follows practically the same course as does the Hansa yellow.

For the blue-green I find that the purest form of iron blue or Prussian blue, potassium ferric ferrocyanide, called by artists' colourmen "Chinese blue," is very satisfactory. In integral colour it appears too blue, but when it is examined spectro-photometrically (figure 7) the reflecting power is found to be not only higher in the deep blue but also higher in the green than the Glacier blue lake, and in addition the pigment is free from the band of reflection in the deep red. In spite, therefore, of its too blue integral colour and low reflecting power in the green, it is a nearer approximation to a minus red than is the better-appearing blue-green lake first chosen.

With this palette—extra pale cadmium yellow, Chinese blue, and a phosphomolybdo-tungstic acid lake of Rhodamine 6-G—together with zinc white as the base, I have done a great deal of painting, and some has been done by several artists whom I have been able to interest in the problem. It proves to be adequate to handle the vast majority of colours needed for naturalistic painting. In combination these colours give an excellent black; in mixtures two by two they give good reds and greens. The blues, because of the deficient reflection of both the Chinese blue and the Rhodamine lake, are not as bright as the best cobalt or ultramarine blues. A condition which makes these defects of relatively small importance is that practically all colours of natural objects are extremely unsaturated. It is practically always necessary to use some admixture of white to match the colours one desires to copy.

A few words may be said at this point in regard to the technique of three-colour painting in oils by the use of the pigments just described. The outstanding difference between the ordinary oil technique and this special one is that in place of a dozen or more pigments being placed on the palette there are only four, namely the white, which is to be made the subject of absorption, and the three subtractive primaries. It is important to keep these colours clean and free from contamination by the others. My own practice has been to use a set of four small palette knives to transfer the pigments from their original piles to a portion of the palette where they are mixed, the mixing then being done either with another knife or with the brush. Another procedure is to lay out the special colours in a series of quite small piles which can be picked up one by one with a brush or palette knife without disturbing the others. In general, because of the great saturation of these colours and their wide difference in character from any which occur in the final picture, a considerable amount of mixing is necessary before the actual colour laid on the canvas is attained. The technique which has just been described differs considerably



from the practice of many artists who form their mixtures as they paint, with the brush, which makes possible great speed of attack. This practice is aided by the comparative impurity of the ordinary artist's colours, and the consequent rather small amount of mixing which is called for. The procedure best fitted for the use of the three-colour palette is still in a state of flux, but experience thus far has indicated that its special requirements can be readily adapted to effective painting with a great shortening of the process of learning the method of getting the desired colours.

§ 5. DISCUSSION

I conclude my presentation of the theory and experimental realization of a method of trichromatic painting in oil* by a discussion of the researches necessary to its full perfection, and by a discussion of the advantages and merits of the method.

The future technical work needed follows from the comments already made on the pigments now available. Taking these up in turn, we note that the yellow at present used, namely extra pale cadmium yellow, is very satisfactory, and is probably as close an approximation to the ideal as may reasonably be expected. A defect is that it is an opaque colour, while the other two are transparent, which results in the blacks being unbalanced and going purple instead of grey on dilution with white. A possible improvement would be the substitution of a transparent yellow of high colouring-power. Turning next to the minus green, for which a tungstic acid lake of Rhodamine 6-G is used, we note two deficiencies. First, the reflecting power for the blue of the spectrum is too low, a defect which is accentuated as the concentration is increased; this pigment in fact becomes red with concentration instead of remaining crimson. Secondly, while remarkably permanent for colours of this nature, it is nevertheless subject to slow change on exposure to light. A principal problem for research is therefore the production of a crimson having the general characteristics of this one, but of higher blue reflecting power and of greater permanence†.

* Although my own painting experiments have been confined to oil colours, I have investigated water colours to the extent of looking over the water-colour paints put out by several manufacturers. Of these a pale cadmium and a Prussian blue are practically identical with the oil pigments I have used. The Rhodamine 6-G lake is obtainable as a water paste, which has very similar working properties to the water colours sold in tubes. Experiments on mixing these show that excellent matches can be made with all the colours usually included in a water-colour box. The substitution of water for the yellow oil medium results in a notable improvement over the oil mixtures in the blues. In working with aquarelle these three colours are all that are needed, as the white is that of the paper used.

† The best samples of Rhodamine 6-G lake compare favourably in permanence with the madder lakes, very widely used and approved by painters. According to Laurie these "fade slowly when exposed to light, but are sufficiently permanent for all practical purposes." Quite marked differences in fastness to light are found in lakes of the same composition, but from different sources. This fact offers promise that further research into methods of manufacture will yield material improvements in permanence. Such research, directed intensively to the few pigments called for by the three-colour palette, has greater chance of success than a diffuse attack on the whole problem of the permanence of dyestuff lakes. A possible help in improving the permanence of pigments of this class is the admixture of a considerable fraction of some permanent pigment of approximately the same colour. For instance, cobalt violet, figure 12, is suitable for using with the Rhodamine lakes. Alone it is not sufficiently saturated but in the mixture it carries part of the colour and acts as a partial light shield to the lake.

Of the three pigments the minus red is furthest from the ideal and constitutes the most difficult problem. In the dyestuff field an apparently universal characteristic of the blue-greens is that they derive their colour from two absorption bands, one in the yellow and another in the violet. They thus exhibit two reflecting regions, one in the deep red and one in the blue-green of the spectrum, and this latter band is too narrow for our purpose. Both the spectrum blue and the spectrum green, which should be present undiminished, are deficient. Consequently the blue obtained by mixing such a pigment with crimson is too dull, as compared for instance with ultramarine, and the greens obtained by mixing with yellows are not so brilliant as, for instance, emerald green. In the field of inorganic colouring materials I have not as yet been able to find a satisfactory pigment. A promising line of attack appears to lie in the copper compounds. Thus the beautiful blue-green obtained by colouring the proper kind of glass with copper, of which transmission curves are shown in figure 7, would be highly satisfactory if it could be secured in a form suitable for grinding with linseed oil. As yet, however, it has not proved possible to colour a glass nearly deeply enough to make it a good pigment when powdered. What is needed here is a compound similar to cobalt blue in which the colouring material is copper instead of cobalt, or a compound similar to the iron blues but coloured with copper. This is a problem which I recommend for study to colour chemists.

Before we leave the subject of pigments for three-colour painting a few words may be said on the subject of variations or compromises on the simple three-colour palette which might be worthy of consideration. These are of two classes; first, such compromises as may be forced by an impasse in the effort to meet the specifications indicated by theory, and secondly, such as may simplify the practical use of the method. Under the first class I may mention the possibility of using more than one pigment for each of the minus colours. The object of this would be to prevent those losses of luminosity and saturation which are due, as discussed above, both to the use of a continuous-spectrum white and to the characteristics of available pigment absorption bands. The pigment for which a substitution of two or more is most likely to be advantageous is the minus green. The Rhodamine 6-G lake, as shown in figure 8, falls off badly in reflecting power on concentration at the red and even more at the blue end of the spectrum, necessitating a lowered key for the whole painting where bright reds and still more where blues occur. The suggested compromise would be to substitute for the single pigment a pair, "warm" and "cold," one with its absorption band more toward the blue the other toward the red. In this case the pair might consist of the two Rhodamines, 6-G and B, if these can be produced of sufficient permanence. Figure 12, giving spectro-photometric reflecting-power curves for these two pigments, illustrates this point*. Another way

* The importance of the minus greens in subtractive painting is probably not generally realized by artists. These colours do not often occur as such except in flowers, and are very poorly represented in the traditional pigments. Their use in mixtures to give greys, browns and blues is not obvious from their very different appearance from these colours. Their importance will be understood upon outlining the characteristics of a full subtractive palette drafted with no reference to the simplifications made possible by the three-colour principle. Such a palette, illustrated in figure 12, would consist of a series of narrow juxtaposed intense absorption bands, which together would absorb the entire

to offset the deficiency of this crimson would be to use with it an additional minus red and minus blue which demand a lower concentration of the crimson in their mixtures. This would mean a more orange yellow, such as aurora yellow, and a bluer minus red, such as a greenish ultramarine. A complete duplicate three-colour palette might consist of strontian yellow and aurora yellow for the minus blues, Rhodamine B and 6-G lakes for the minus greens, and two minus reds, one a greenish ultramarine, the other some as yet unavailable copper compound of the

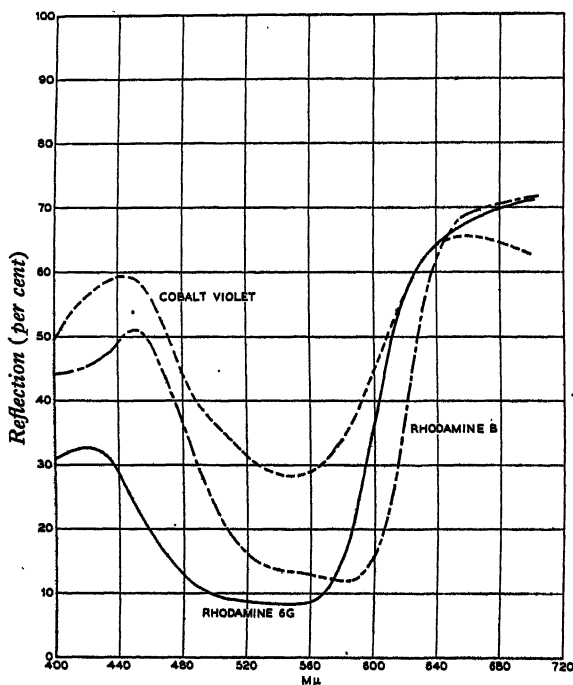


Figure 12. Reflecting power of two Rhodamine lakes, illustrating the use of two available pigments to cover the range demanded theoretically from one.

kind previously discussed. Such a duplicated palette would give an exceedingly rich set of mixed colours. It would, however, be purchased at the sacrifice of the simplicity and freedom from ambiguity of the simple three-colour palette, reasonably ideal pigments for which, it is hoped, will be ultimately available. I consider it unlikely that any greater complication than the suggested use of two minus greens need be contemplated.

The second possible variation of the three-colour palette is in practices which may simplify the technique. Of these I select the use of a series of neutral greys spectrum. Of these the two extremes would be a lemon yellow and a light blue-green. All the others would be crimsons, purples and pinks. This complete subtractive palette may be contrasted with the "spectrum" series of pigments, put out by some colourmen, which are approximately of the principal hues of the spectrum, and obviously inspired by ideas only appropriate to additive colour mixture. A true spectrum palette of this latter sort would permit no mixtures except with white, and must be continued beyond the spectrum through a series of purples, thus demanding more pigments than the subtractive one above described; and this in turn is, as the three-colour principle shows, more extensive than necessary.

instead of white as the base from which to absorb light. By reference to the colour cube, figure 1, it is evident that instead of arriving at a colour in the cube by absorbing red, green and blue by working back from the white vertex, one could start with the proper point on the black-white or grey line, and use only two of the coloured pigments. Stated in terms of mixing technique, this means that the mixing-table or palette might display the three minus colours and a series of greys, the latter made by previously mixing white with the three coloured pigments, or by mixing white and some neutral black, such as ivory black*. The hue of the desired colour would then be obtained by mixing two of the coloured pigments, its value and saturation by choice of the proper grey. The same result is also obtained if we make

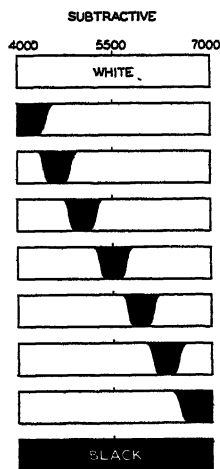


Figure 13. Characteristics of a complete subtractive palette disregarding the simplifications made possible by the three-colour principle.

our palette of the three coloured pigments, white and black. The practical simplification introduced by this procedure lies in the fact that the process of darkening a colour is such a constantly recurring and fundamental problem as to deserve a simple solution. Where it is done by adding all three minus pigments, the hue is apt to be thrown violently this way and that before the apparently simple change is made. The use of black is thus not a theoretical requirement but a working simplification comparable to the use of vectors as contrasted with Cartesian co-ordinates.

In conclusion I wish to stress the practical advantages and the philosophical merits of the method of painting I am advocating. The great advantage of the three-colour system is the reduction in the number of pigments necessary, and the simplification of the procedure of mixing colours. The mere reduction in the number of pigments used diminishes the likelihood of alteration with the passage of time in the pictures painted. It has long been commented upon by students of old paintings

* The practical advantage of using a simple black lies in the fact, already noted, that the three pigments now available are of different transparency, so that the black obtained by their mixture does not remain neutral on simple dilution with white. In making a series of greys the proportions of the pigments have to be continuously altered.

that many world-famous masterpieces have suffered serious alteration in appearance because the numerous pigments used in them have changed at different rates and directions owing to their chemical interaction and the effects of light. Spots of reflected light painted with an earth colour become, for instance, brighter than the primary source painted in a lake. Pictures noted originally for brilliant flesh tints are now admired for their monotone modelling. With the number of pigments limited to the irreducible minimum and research concentrated on the qualities of these, the likelihood of such changes should be notably reduced. As to the procedure in mixing pigments, whereas with the artists' pigments now in use the number of ways of arriving at a given colour (provided that it can be made) is enormous, with the three-colour palette there is just one way to mix each colour, and with a perfected three-colour palette there will never be any question as to whether the colour can be secured. The way to obtain a given colour is furthermore clearly indicated once the underlying theory is grasped.

This latter point leads to what is perhaps the most important philosophical merit of the three-colour palette. This is that by its use the theory of the mixture of pigments, and the education of artists in colour, are directly correlated with the theory of colour as understood by scientific students of optics. It may be safely said that at present there is no such correlation; that the theory of colour as produced by light is commonly not understood by artists, and is widely believed to be unconnected with the mixture of pigments. This latter belief is, of course, erroneous but is quite comprehensible as long as artists work with pigments which have no scientific basis.

The teaching of colour to artists need not be extended to the complete theory as here developed. I find that a quite sufficient guide to the use of the three colours is obtained by picturing the spectrum on a colour triangle, such as figure 2 *b*, with white at the centre, the third side giving the purples, and indicating by three arrows the positions of the three pigments at the sides of the triangle. A student needs merely to be told to pick out the spectrum hue of the colour he wishes to paint, and then the colours which must be mixed to produce that hue are those whose arrows lie nearest. The ability to pick the spectrum hue of a colour is quickly acquired. Tints are then made by admixture with white, and general darkening of the colour is produced by an admixture of all three or black. Devices such as superposable transparent wedges of the three minus colours also suggest themselves as possible means by which the artist of the future may be led swiftly and surely to the mastery of the purely mechanical phase of his craft.

As a final word, let me emphasize that what I have here presented is in the nature of a preliminary survey of the problem. It represents spare-time study extending over about a year, and as such cannot pretend to any finality. New pigments and new techniques in painting must be exhaustively tested by all the resources of the chemist, and particularly by the passage of time. I believe, however, that the investigation has been carried sufficiently far to show that the three-colour principle of Thomas Young is capable of materially simplifying and advancing the painter's craft. It is my earnest hope that the subject may be taken up seriously by some properly equipped research body, with the backing of some academy or other institution of art.

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THE RECTIFYING PEAK VOLTMETER AS A STANDARD INSTRUMENT

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ABSTRACT. The paper describes a peak voltmeter using overbiased rectifying valves. Various errors are discussed and calculated.

§ 1. INTRODUCTION

THE rectifying peak voltmeter has been described by Chubb and Fortescue*. The voltage is applied across a condenser C and a pair of rectifiers, as shown in figure 1. The rectifiers are a pair of contacts which make and break simultaneously, so that only one of the pair is closed at any moment. An ammeter A is placed in one arm and measures the current that passes through one rectifier. If the wave is periodic and vanishes at equal time intervals, it is possible to time the make and break so that the positive charging current (half the sine wave) will go through rectifier 1 and the negative through rectifier 2. For this method to be possible it is necessary that there should be no even harmonics, or else the wave will not vanish at equal intervals of time, the duration of the positive part of the wave being different from that of the negative.

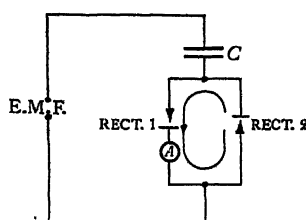


Figure 1.

In order to overcome this awkward restriction the mechanical contacts have been replaced by thermionic diodes, but the following errors are immediately introduced. There is an error due to the fact that diodes will give an emission current of about 2 per cent of their normal value, even when no voltage is applied to the anode, so that even when no e.m.f. is applied to the system in figure 1 a circulating current will flow in the direction shown. Moreover diodes have finite and variable

* *Trans. Am.I.E.E.* 32, 739 (1913).

impedances. Corrections can be calculated* but the calculation is irksome and the correction depends upon the valve characteristic; indeed it is difficult to say of what order the error is likely to be for various applied voltages and diode characteristics, especially as the characteristics vary with time. It is possible to suppress the circulating current by applying bias batteries B^\dagger , as shown in figure 2. Thus, if curve 1 in figure 3 shows the (emission current, anode volts) characteristic for each unbiased diode, curve 2 is the characteristic for a suitable bias; and if this curve were a straight line and fixed in time the method would be satisfactory. If

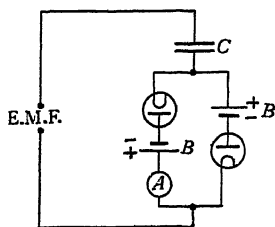


Figure 2.

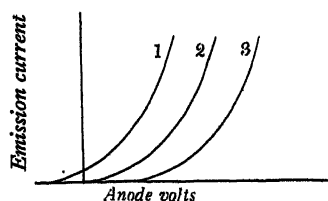


Figure 3.

the bias is excessive, on the other hand, the characteristic for each diode is shown by curve 3. It has generally been assumed that this latter state is undesirable, but it will be shown that, far from being undesirable, it is the best arrangement. It reduces the errors due to the diode impedances to a very small amount which is easily calculated within narrow limits, and, although the characteristics and biases may vary with time, the errors will always remain less than some preassigned negligible quantity. The instrument may, in fact, under these conditions be used as a standard without the necessity of continual recalibration.

The arrangement is portable and robust.

§ 2. THE MODIFIED PEAK VOLTMETER

The arrangement is shown in figure 4. The high voltage is applied across the standard air condenser and the rectifying system (shown in a rectangle) in series. The valves are triodes, Marconi-Osram DL, d.c., indirectly heated, and require 0.25 A. at 16 V. They were chosen because of their good insulation between heater and cathode, since the cathodes may have a voltage-difference of 100 V. and the heaters are nearly at the same voltage. The valves are heated with a.c. at 50 ~ at 230 V., transformed down to approximately 16 V. by a Heayberd transformer with a ratio of 250:18. The small resistance r is inserted to produce the correct current in the heaters. A is a standard micro- or milliammeter. A safety (neon) gap is placed across the device in case of a failure.

* R. Davis, G. W. Bowdler and W. G. Standring, *J. Inst. E.E.* 68, 1228 (1930).

† See *Methods of High Voltage Measurement* by S. Whitehead, L./T. 55, British Electrical and Allied Industries Research Association, p. 47.

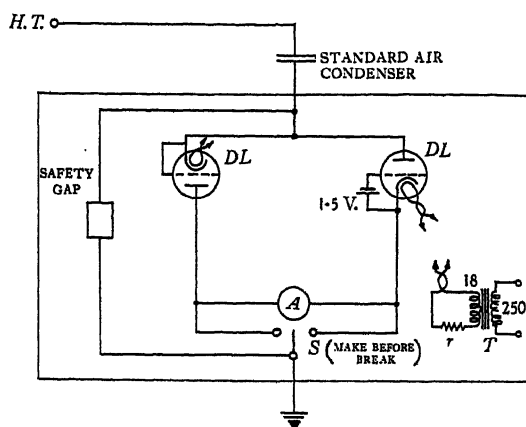


Figure 4.

In one valve the grid is connected to the cathode, whilst in the other a grid-bias of about -1.5 V. is used in order to suppress the circulation current. Table 1 gives the values of circulating current for different values of the grid-bias in this valve.

Table 1.

Grid-bias (V.) negative	0	0.2	0.4	0.6	0.8	1.0	1.2	1.5
Circulating current (μ A.)	280	230	110	56	22	7	0	0

It is seen that the correct bias for the suppression of the circulating current is 1.1 V., but it will vary a little from valve to valve. It will be shown in appendix 1 that overbiasing produces no appreciable error in the instrument. A variable grid-bias is cumbersome and quite unnecessary, but it is easy to put a small dry cell of 1.5 V. between the grid and the cathode.

Assuming that the biasing is perfect and the diode impedances zero, the simplified theory of the instrument is as follows. The voltage to be measured charges up the capacity C . When the voltage decreases continuously from V_{\max} to $-V_{\max}$, the charging current goes down through the left-hand diode and the total charge that flows is $2CV_{\max}$. If the fundamental frequency of the wave is f , this happens f times per second, so that the mean current i_g in the galvanometer is given by

$$i_g = 2fCV_{\max} \quad \dots\dots(1).$$

Therefore

$$\left. \begin{aligned} V_{\text{rms}} &= V_{\max}/\sqrt{2} \\ &= i_g/2\sqrt{2}fC \\ &= (\pi/\sqrt{2}) i_g/\omega C \\ &= 2.22 i_g/\omega C \end{aligned} \right\} \quad \dots\dots(2),$$

where

$$\omega = 2\pi f.$$

Equation (1) holds for any wave, provided it vanishes at equal time intervals and has only one maximum and one minimum per cycle. Equation (2) holds only for a pure sine wave, since it assumes that $V_{\text{rms}} = V_{\text{max}}/\sqrt{2}$.

§ 3. ERROR DUE TO OVERBIASING

Suppose curve 1 in figure 5 is the characteristic for one diode and curve 2 for the other, where these curves are straight lines that meet the axis of voltage at $+e$ and $-e$. In practice the curves will not be straight lines, but the deviation will be considered in a moment and shown to be negligible. The combination of the diodes acts like a constant resistance, which requires a flash-over voltage. If i is the current and v the voltage across the rectifiers,

$$\begin{aligned} & \text{and} \quad \left. \begin{aligned} v &= e + Ri, \text{ for } i > 0 \\ v &= -e + Ri, \text{ for } i < 0 \end{aligned} \right\} \quad \dots\dots(3). \\ & \text{For} \quad -e < v < e, \quad i = 0 \quad \dots\dots(4). \end{aligned}$$

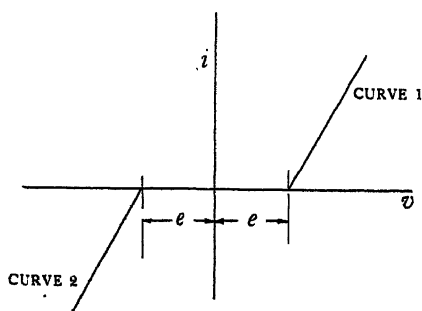


Figure 5.

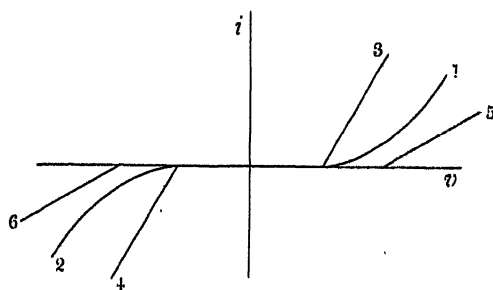


Figure 6.

It is proved in appendix 1 that the error in peak-voltage reading is given by

$$\text{so that the error is} \quad \frac{1}{2} (\omega CR)^2 V_{\text{max}} + e \quad \dots\dots(5),$$

$$\left[\frac{1}{2} (\omega CR)^2 + (e/V_{\text{max}}) \right] \times 100 \text{ per cent} \quad \dots\dots(6).$$

If the characteristics are curves, as shown by curves 1 and 2 in figure 6, it is clear that the meter will read more than if the characteristics were 5 and 6, but less than if they were 3 and 4. If curves 3 and 4 have intercepts $\pm e_1$ and slope R_1 and curves 5 and 6 have intercepts $\pm e_2$ and slope R_2 , the error in the actual case lies between

$$\left[\frac{1}{2} (\omega CR_1)^2 + (e_1/V_{\text{max}}) \right] \times 100 \text{ per cent and } \left[\frac{1}{2} (\omega CR_2)^2 + (e_2/V_{\text{max}}) \right] \times 100 \text{ per cent} \quad \dots\dots(7).$$

The values of e and R were found roughly for the practical arrangement shown in figure 4. Figure 7 is a graph of v plotted against i , and it is found that

$$\begin{aligned} & \text{and} \quad e = 13 \text{ V.}, \\ & \quad \quad R = 4400 \Omega. \quad \dots\dots(8). \end{aligned}$$

At 50 ~ and with a condenser of 100 $\mu\mu\text{F}$., $\omega CR \approx 10^{-4}$, so that the error due to the impedance is of the order 10^{-6} per cent, which is quite negligible. The error due to overbiasing is then a constant, namely e . That is to say, that no matter what

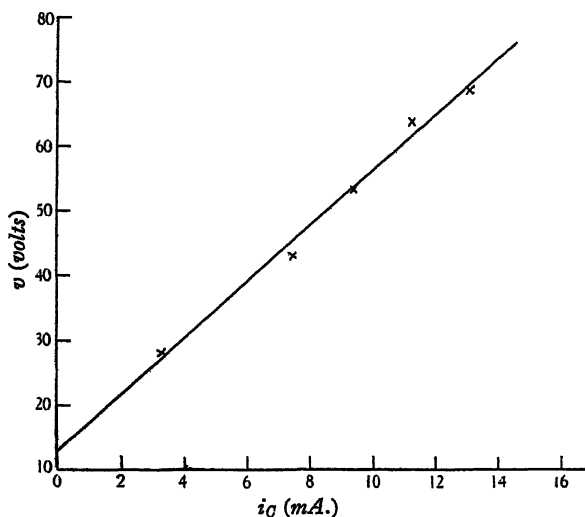


Figure 7.

voltage may be applied, the peak is underestimated by the constant e which equals 13 V. nearly. We can get the true peak by adding e to the voltage $i_g/2fC$, so that

$$V_{\text{peak}} = (i_g/2fC) + e \quad \text{.....(9),}$$

or

$$V_{\text{rms}} = (\pi/\sqrt{2}) i_g/\omega C + e/\sqrt{2} \quad \text{.....(10).}$$

Tests were made with the results shown in table 2.

Table 2.

Kilovolts (r.m.s.) applied to primary transformer winding and standard voltmeter	i_g (μA .)	$2.22 i_g/\omega C$	$2.22 i_g/\omega C$ + $e/\sqrt{2}$	Error (per cent)
1.00	34.2	982	991	- 0.9
2.00	69.5	1992	2001	0.0
3.04	105.5	3050	3059	+ 0.6
4.04	140.0	4020	4029	- 0.3
5.06	177.0	5080	5089	+ 0.6
6.10	212.0	6090	6099	0.0
7.16	248.0	7140	7149	- 0.1
8.20	282.0	8100	8109	- 1.2
9.26	320.0	9200	9209	- 0.55

$C = 246 \mu\mu\text{F}$. for the standard condenser.

Even if the error e due to overbiasing is neglected, the error above 2 kV. is very small, about 0.4 per cent. If no biasing is used, the circulating current is

280 μA . which corresponds to an applied voltage of 8.2 kV. The overbiased arrangement thus enables comparatively low voltages of 2 and 3 kV. to be read accurately. Very high voltages will be read accurately on the under- and over-biased arrangements, but the latter extends the range right down to 2 kV. With a condenser of 246 μF ., the overbiased voltmeter will read accurately from 2 kV. to 500 kV., but it is not quite certain when the underbiased voltmeter will begin to be accurate. This will be investigated in the next section, but before this is done a surprising fact must be explained.

Suppose 2 kV. (r.m.s.) is applied to the voltmeter. The galvanometer current is about 70 μA . and the condenser current is 2.22×70 or 155 μA . (r.m.s.). This means that the voltage across the diodes is never more than 15 volts, whilst no current flows when the voltage is less than 13 volts. One would expect that the error would be of the order 1300/15 per cent or 80 per cent. The reason why the error is small is this: when the alternating e.m.f. is in series with the condenser C and resistance R , the current leads the voltage by nearly 90° if ωCR is small. The voltage across the resistance (here the rectifiers) is proportional to the current, and is a minimum when the applied e.m.f. is a maximum. This is due to the fact that the condenser is fully charged at this moment, and the potential of charge opposes the applied e.m.f. almost completely. If the rectifiers will not pass current when the voltage lies between $-e$ and $+e$, the charge and potential difference of the condenser remain constant for a time, whilst the applied e.m.f. must change by $2e$; and as the condenser charge remains unaltered, the voltage across the rectifier changes by $2e$ also in this time. It takes only a very short time for the e.m.f., $V_{\max} \cos \omega t$, to vary through a voltage $2e$ in the neighbourhood of its maximum, the time being approximately $4\omega^{-1} \sin^{-1} \sqrt{(e/2V_{\max})}$ sec. or $2\pi^{-1} \sin^{-1} \sqrt{(e/2V_{\max})}$ of a cycle. If e is small compared with V_{\max} , as it is, current does not flow for $\pi^{-1} \sqrt{(2e/V_{\max})}$ of a cycle. If $e = 13$ and $V_{\max} = 2000\sqrt{2} = 2820$, this is only 1/30 of a cycle, so that current is suppressed only for a short time. Also the current that should flow is small in comparison with the mean current, so that the error is very small.

§ 4. ERROR DUE TO CIRCULATING CURRENTS

In order to see the effects of circulating currents, various voltages from 20 to 90 kV. were applied with grid-bias -1.5 and grid-bias 0. The capacity of the standard condenser was, in this case, 100 μF . First it was verified that the grid-bias -1.5 V. suppressed the circulating current entirely, and it was assumed then that this arrangement gave the correct result. The voltmeter in the primary supply was not at all accurate, but served merely as an indication of the order of the applied voltage. Then the galvanometer readings for biases of -1.5 V. and 0 V. were found for voltages 20 to 90 kV. The error due to the circulating current was then found to be as shown in table 3.

Table 3.

Applied kilovolts (approximate)	i_g ($\mu\text{A.}$)		Error (per cent)
	Bias - 1.5	Bias 0	
20	252	296	17.5
30	416	442	6.25
40	540	559	3.5
60	822	830	0.97
80	1086	1093	0.645
90	1220	1230	0.82

It seems then that the underbiased system cannot be used for voltages less than 100 kV. without an error of nearly 1 per cent, whereas the overbiased system can be used down to 2 kV.

§ 5. ERROR DUE TO MULTIPLE MAXIMA AND MINIMA

Suppose the wave is of the shape shown in figure 9. Then the voltage that will be measured will be $(v_1 - v_2) + (v_3 - v_4) + (v_5 - v_6)$, since each of these downward steps will send charging current through the same diode. The measured voltage is thus

$$(v_3 - v_6) + (v_1 - v_2) + (v_5 - v_4),$$

instead of $(v_3 - v_6)$, which is the difference in peaks. The voltmeter will thus over-estimate the peak voltage.

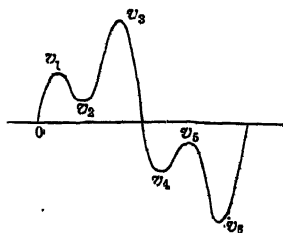


Figure 9.

There are various causes that produce multiple maxima and minima. One cause is bus-bar discharge. It was found, however, that it required a considerable artificial discharge, much in excess of what will ordinarily happen, to cause an increase of reading on the overbiased voltmeter. It is not known, but it is expected, that overbiasing helps here too. If the discharge voltage is less than e it will be ignored, whereas in the unbiased instrument any discharge voltage will have an effect which will be greater the higher the frequency of the discharge, since condenser current is proportional to frequency.

Error due to third harmonic. A third harmonic, provided it is large enough and has the requisite phase, can cause multiple maxima and minima. Phase is important, as can be shown by taking the two simple cases of figures 10 and 11. In figure 10

the fundamental is $E \sin \omega t$ and the harmonic is $E_3 \sin 3\omega t$, say. The condition for multiple maxima and minima is that

$$\frac{d}{dt}(E \sin \omega t + E_3 \sin 3\omega t) = 0$$

should have real roots apart from $\omega t = \frac{1}{2}\pi$. The equation is

$$\begin{aligned} 0 &= E \cos \omega t + 3E_3 \cos 3\omega t \\ &= \cos \omega t [E + 3E_3 (4 \cos^2 \omega t - 3)], \end{aligned}$$

giving

$$4 \cos^2 \omega t = 3 - E/3E_3.$$

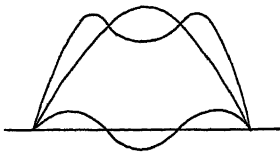


Figure 10.

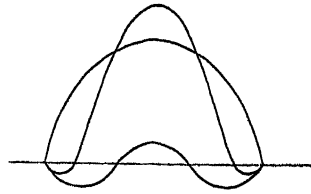


Figure 11.

For real roots,

$$3 - E/3E_3 > 0,$$

or

$$E_3 > \frac{1}{3}E,$$

so that multiple maxima and minima will occur for a harmonic greater than 11 per cent.

It is clear that in the case shown in figure 11 the condition for multiple maxima is that the equation

$$4 \cos^2 \omega t = 3 + E/3E_3$$

should have real roots, so that $E/3E_3 + 3 = 4$, and $E_3 = \frac{1}{3}E$; i.e., a harmonic of 33.3 per cent is required.

Suppose the fundamental is $E \sin(\omega t + \alpha)$ and the harmonic is $E_3 \sin 3\omega t$. We may call α the "phase difference" between these waves, but it must be remembered that this definition is arbitrary. To cover all possible cases it is sufficient to take α between 0 and $\pi/3$, for if α is negative, we may reverse the sign of α and obtain the wave reversed in time; if α is greater than $2\pi/3$ or $4\pi/3$ we may subtract $2\pi/3$ or $4\pi/3$, for this means starting one or two cycles later in the third-harmonic wave; and if α lies between $\pi/3$ and $2\pi/3$, we can subtract $2\pi/3$, obtaining an angle between 0 and $-\pi/3$, whose sign we may reverse. Thus in all cases we can put $0 - \alpha - \pi/3$. The wave is then

$$E \sin(\omega t + \alpha) + E_3 \sin 3\omega t \quad \dots\dots(11).$$

The r.m.s. value of the wave is

$$\sqrt{(E^2 + E_3^2)} \quad \text{or} \quad E\sqrt{1 + (E_3/E)^2},$$

which is approximately $E(1 + E_3^2/2E^2)$. This is independent of α , the phase.

Figure 12 gives the ratio of peak to fundamental peak for various magnitudes and phases of third harmonic. In the cases of $\alpha = 0$ and $\alpha = 10^\circ$ multiple maxima

occur and the rectifier reading is greater than the actual peak. Even with this effect, for $\alpha = 0$, the rectifier reading is less than the peak of the fundamental for harmonics up to 23.5 per cent.

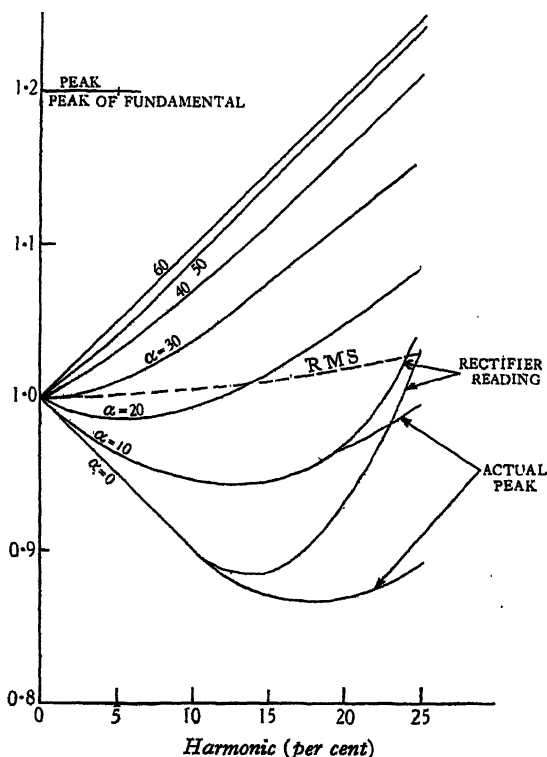


Figure 12.

§ 6. ERROR DUE TO CAPACITY ACROSS RECTIFIERS

Suppose that the screened leads that connect the standard condenser C to the rectifiers have a capacity C_1 connected across the rectifiers, as shown in figure 13. This capacity will shunt some current from the rectifiers and will cause an error, which may be calculated very quickly by the use of Thevenin's theorem*.† By this

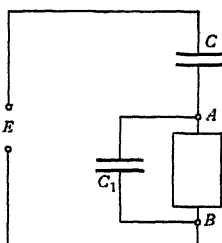


Figure 13.

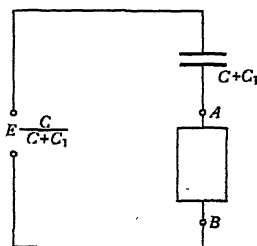


Figure 14.

* Shea, T. E., *Transmission Networks and Wave Filters*, p. 55.

theorem, we may replace the whole of the system to the left of AB by the e.m.f. across AB when the rectifier system is absent, and a series impedance equal to that looking left from AB , when the source of e.m.f. is short-circuited.

The e.m.f. across AB when the rectifiers are absent is $EC/(C + C_1)$. The impedance looking left is that of condensers C and C_1 in parallel. Thus the effect of C_1 is to reduce the e.m.f. to $EC/(C + C_1)$ and increase the capacity to $(C + C_1)$, figure 14. The charge is $[EC/(C + C_1)] \times (C + C_1)$ or EC , so that if the rectifiers had no impedance the error would be zero. As it is, the error increases from $\frac{1}{2}(\omega CR)^2 E$ to $\frac{1}{2}(\omega \cdot \overline{C + C_1} \cdot R)^2 E$. The former is negligible and the latter is nearly $\frac{1}{2}(\omega C_1 R)^2 E$, so that the error is $\frac{1}{2}(\omega C_1 R)^2 \times 100$ per cent. With ω equal to 314 and R to 4000Ω , if an error of $\frac{1}{2}$ per cent is permitted we can tolerate

$$(\omega C_1 R)^2 \times 100 = 1,$$

$$\omega C_1 R = \frac{1}{10},$$

$$C_1 = 1/10 \omega R = \frac{1}{12} \mu\text{F. approximately.}$$

§ 7. ACKNOWLEDGMENTS

The author wishes to thank Dr L. G. Brazier for much helpful criticism and advice; and Callender's Cable and Construction Co., Ltd. for permission to publish this work, which was done in the Company's research laboratories at Wood Lane.

APPENDIX 1

Suppose that a voltage $E \sin(\omega t + \theta)$ is applied in series with a condenser C and the rectifying system. The condenser plates have charges $+q$ and $-q$, the current is i and the voltage across the rectifying system is v . Then

$$i = dq/dt.$$

The rectifiers are overbiased so that no current passes unless v is greater numerically than e .

Then

$$v = e + Ri, \text{ for } i > 0$$

$$e \leq v \leq e, \text{ for } i = 0,$$

and

$$v = -e + Ri, \text{ for } i < 0.$$

Everything is anti-symmetrical in the two half-cycles.

Figure 8 shows the charge and current as functions of time. We have the equation

$$E \sin(\omega t + \theta) = (q/C) + v \quad \dots\dots(1),$$

which holds throughout, and the following additional equations which hold in the specified intervals of time.

Intervals	Equations	
(a) $t_2 - \pi/\omega < t < t_1$	$i > 0. v = e + R dq/dt$	$\dots\dots(2),$
(b) $t_1 < t < t_2$	$i = 0. dq/dt = 0$	$\dots\dots(3),$
(c) $t_2 < t < t_1 + \pi/\omega$	$i < 0. v = -e + R dq/dt$	$\dots\dots(4),$
(d) $t_1 + \pi/\omega < t < t_2 + \pi/\omega$	$i = 0. dq/dt = 0$	$\dots\dots(5).$

There are the following boundary conditions:

$$\text{At } t = t_2 - \pi/\omega, \quad i = 0, \quad v = e, \quad q = -Q \quad \dots\dots(6),$$

$$t = 0, \quad q = 0 \quad \dots\dots(7),$$

$$t = t_1, \quad i = 0, \quad v = e, \quad q = Q \quad \dots\dots(8),$$

$$t = t_2, \quad i = 0, \quad v = -e, \quad q = Q \quad \dots\dots(9).$$

In the interval (a), we have from equations (1) and (2)

$$E \sin(\omega t + \theta) = (q/C) + e + R(dq/dt),$$

giving

$$q = A \exp.(-t/CR) - Ce + CE [1 + (\omega CR)^2]^{-1/2} \sin(\omega t + \theta - \alpha) \quad \dots\dots(10)$$

where

$$\alpha = \arctan \omega CR.$$

Then

$$i = -(A/CR) \exp.(-t/CR) + \omega CE [1 + (\omega CR)^2]^{-1/2} \cos(\omega t + \theta - \alpha) \quad \dots\dots(11).$$

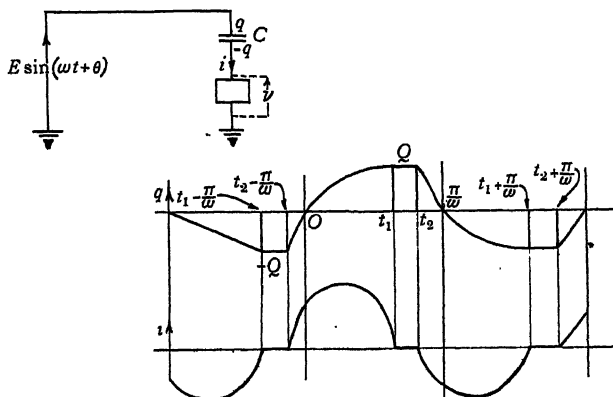


Figure 8.

In the interval (b)

$$dq/dt = 0.$$

So that

$$q = \text{constant} = Q, \text{ say,} \quad \dots\dots(12),$$

and

$$i = 0.$$

Because of the skew symmetry, we need not consider any other intervals.

Equations (6) and (11) give

$$0 = -(A/CR) \exp. [(\pi - \omega t_2)/\omega CR] + \frac{\omega CE}{\sqrt{1 + (\omega CR)^2}} \cos [(\omega t_2 + \theta - \alpha - \pi)].$$

Equations (8) and (11) give

$$0 = -(A/CR) \exp. [-\omega t_1/\omega CR] + \frac{\omega CE}{\sqrt{1 + (\omega CR)^2}} \cos [\omega t_1 + \theta - \alpha].$$

By division, these last two equations give

$$\exp. [(\pi + \omega t_1 - \omega t_2)/\omega CR] = \cos(\omega t_2 + \theta - \alpha - \pi)/\cos(\omega t_1 + \theta - \alpha) \quad \dots\dots(13).$$

Equation (6) gives also

$$e = E \sin(\omega t_2 - \pi + \theta) - (-Q)/C,$$

or

$$e = -E \sin(\omega t_2 + \theta) + Q/C \quad \dots\dots(14).$$

Equation (8) gives

$$e = E \sin(\omega t_1 + \theta) - Q/C \quad \dots\dots(15).$$

Equations (13), (14) and (15) determine t_1 , t_2 and Q , which are the quantities of interest.

$$\begin{aligned} \text{Let} \quad & \beta = \frac{1}{2}\pi - (\omega t_1 + \theta - \alpha) \} \\ \text{and} \quad & \gamma = (\omega t_2 + \theta - \alpha) - \frac{1}{2}\pi \} \end{aligned} \quad \text{.....(16).}$$

Then equations (13), (14) and (15) become

$$\exp. [(\pi - \beta - \gamma)/\omega CR] = \sin \gamma / \sin \beta \quad \text{.....(13')},$$

$$2e/E = \cos(\beta - \alpha) - \cos(\gamma + \alpha) \quad \text{.....(17)},$$

$$\text{and} \quad \frac{2Q}{CE} = \cos(\beta - \alpha) + \cos(\gamma + \alpha) \quad \text{.....(18)}.$$

Equations (13') and (17) give β and γ , and then (18) gives Q . If the system is correctly biased $e = 0$, and

$$\beta = \gamma = 0.$$

If the system is overbiased, β and γ are positive and small. $\pi - \beta - \gamma > 0$, and in fact $\approx \pi$. Then $\exp. (\pi/\omega CR)$ is very large, since $1/\omega CR$ is of the order of 10,000. Therefore β is very small; in fact we may put it equal to zero.

Equation (17) then gives

$$\cos(\gamma + \alpha) = \cos \alpha - 2e/E,$$

and equation (18) gives

$$\begin{aligned} (2Q/CE) &= \cos \alpha + \cos(\gamma + \alpha) \\ &= 2(\cos \alpha - e/E). \end{aligned}$$

If the rectifier is ideal

$$Q = CE.$$

$$\text{Therefore} \quad Q/Q_{\text{ideal}} = \cos \alpha - e/E.$$

$$\text{Since} \quad \alpha = \arctan \omega CR,$$

$$\begin{aligned} \cos \alpha &= 1/[1 + (\omega CR)^2]^{1/2} \\ &\approx 1 - \frac{1}{2}(\omega CR)^2. \end{aligned}$$

$$\text{Therefore} \quad Q/Q_{\text{ideal}} = 1 - \frac{1}{2}(\omega CR)^2 - (e/E).$$

The error ratio is thus

$$\frac{1}{2}(\omega CR)^2 + (e/E) \text{ or } \delta, \text{ say.}$$

The charge $2Q$ passes through the galvanometer once in each cycle, so that

$$\begin{aligned} i_g &= 2fQ \\ &= 2fCE(1 - \delta), \end{aligned}$$

and the maximum voltage

$$E = i_g(1 + \delta)/2fC.$$

A simpler way of expressing the voltage is

$$E = (i_g/2fC) + e,$$

i.e. the peak voltage is measured e volts low.

If the wave is sinusoidal, the r.m.s. voltage is measured $e/\sqrt{2}$ volts low.

519.24

GRAPHIC STATISTICS

BY A. F. DUFTON, M.A., D.I.C.

Received June 1, 1933. Read October 20, 1933.

ABSTRACT. The plotting of frequency-distributions is discussed. In comparing for different populations the frequency-distributions of a particular variate it is sometimes convenient to take one population as standard and to represent its distribution by a straight line. It is pointed out that the method of plotting individual points described by Hazen is incorrect.

§ 1. PERMILLE PAPER

IN 1914, in a paper on "Storage to be provided in impounding reservoirs for municipal water supply*," Mr Allen Hazen described an elegant method of determining the probability of an event by plotting statistics upon special graph paper†. The method is not very widely known, and in 1930, in ignorance of Hazen's work, I put forward the same method of graphically representing a frequency-distribution. It has the advantage of showing at a glance whether the distribution is normal, and I ventured to give the name *permille* to the co-ordinate paper upon which the curves are plotted‡.

The observations determining a frequency-distribution are usually divided into classes of equal interval, and in this method of representation the figures are added up so as to give a total frequency not exceeding the upper limit of each class interval. Ordinates are then erected on a horizontal base to represent, to a special scale, these integrated frequencies as parts per mille; and a smooth curve may be drawn through the tops of the ordinates. The special frequency scale is the scale of deviates of the normal curve for each permille of frequency§. When drawn to this scale a normal frequency-distribution is of course represented by a straight line.

§ 2. PLOTTING INDIVIDUAL VALUES

With a limited number of observations, just as it is more expedient to find the median by inspection without determining classes of equal interval, so also it is more precise, and sometimes easier, to plot a frequency curve directly from the observed values. Galton's ogive was drawn in this manner||. Furthermore, whatever the number of observations, it is always desirable to plot the outlying values as individual points.

* *Trans. Amer. Soc. Civil Engineers*, 77, 1539 (1914).

† Procurable under the name *Arithmetic Probability Paper*, from Codex Book Co. Inc., Norwood, Massachusetts.

‡ *Phil. Mag.* 10, 566 (1930).

§ *Tables for Statisticians and Biometricians*, p. 1. Printed by Cambridge University Press and issued by the Biometric Laboratory, University College, London.

|| *Phil. Mag.* 49, 33 (1875).

With $(n - 1)$ observations, the frequency curve can be drawn by plotting the r th value in order of magnitude against the ratio r/n^* . This can be shown by Dedekind section, from the inequalities $r/(n - 1) > r/n > (r - 1)/(n - 1)$; for if, for instance, the r th value were plotted against a ratio q less than r/n , it would be possible to find a ratio p , where $q < p < r/n$, which would divide the observations in a ratio greater than or equal to $r/(n - 1)$, and it would follow that $p \geq r/(n - 1) > r/n$, which is absurd.

With nine observations, the values in order of magnitude are plotted against 100, 200, 300, ... 900 per mille. When ninety-nine observations are available, it is generally convenient to plot (on permille paper) every tenth value in order of magnitude together with the five values at each end of the range. This is illustrated in figure 1, which shows a frequency-distribution of the strength of cowhair.

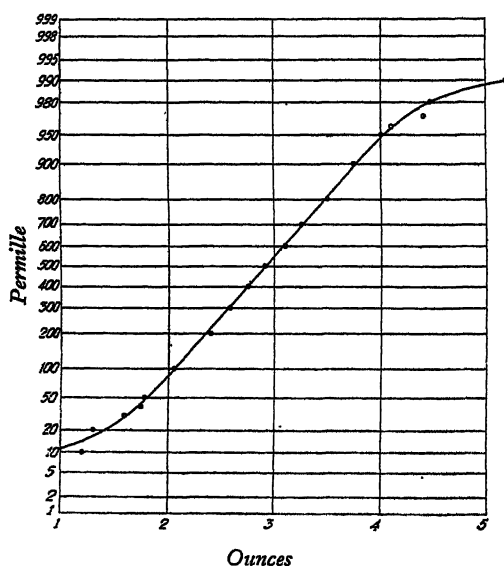


Figure 1.

§ 3. COMPARISON WITH A STANDARD POPULATION

Now it is sometimes necessary to compare for different populations the frequency-distributions of a particular variate and, for this purpose, when the distributions are not normal, a different representation may be convenient, particularly when one population can be regarded as standard.

An attempt to show that capability is in some degree an inheritable character acquired by those of mature years involved the comparison of the frequency-distribution of the paternal age (at birth) for 1000 eminent persons with that for 100,000 children. The first comparison was conveniently made by means of permille

* Mr Hazen falls into error in stating (*loc. cit.* p. 1549) that, if there are 50 terms in the series, the first will be plotted on the 1 per cent line, the second on the 3 per cent line, etc.

paper*, but when the possibility was considered of including in the same diagram the frequency-distributions of the paternal age for other groups of men it became apparent that the comparison would be more apt if the figure were anamorphosed so that the standard curve became a straight line; the comparison is now not with a theoretical distribution but with an actual one.

Such an anamorphosis was, indeed, suggested in my previous paper, the proposal then being to modify the scale of the variate. In general, however, the functional scale so obtained is not simple and the result is not so elegant as that obtained by modification of the frequency scale. The resulting graph is shown in figure 2 and it may be of interest to observe that in this particular example the scale of frequency is substantially logarithmic over the range from 0.01 to 100 per mille.

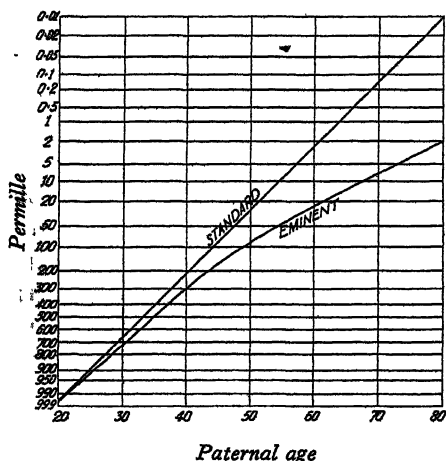


Figure 2.

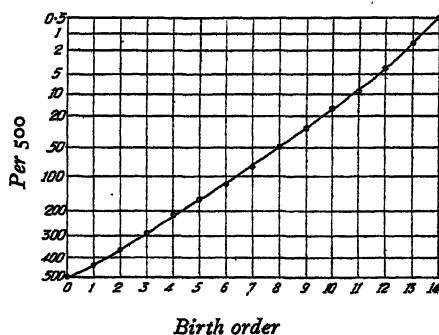


Figure 3.

§ 4. CHOICE OF METHODS

The choice of the various methods of representing a frequency-distribution must of course be made with reference to all the considerations peculiar to a particular case. The distribution of the birth order of children, of which a representation was recently required, affords an illustration of this. A first attempt, made by plotting the individual frequencies upon semi-logarithmic paper, gave quite a good graph, the points appearing to lie upon a parabola. The distribution evidently approximated to one half of a normal frequency-distribution, and I realized that the data might be represented more elegantly upon half a sheet of permille paper as in figure 3, which shows the proportion of children whose birth ordinal exceeds a specified integer.

* *Nature*, 180, 508 (1932).

DISCUSSION

Dr L. E. C. HUGHES. The curves exhibited by the author are similar to those obtained when the distribution of marks in examinations is plotted. The candidates are placed in order along the base of the diagram and given ordinates representing the percentage marks. In marking candidates' work, particularly when different groups of papers are weighted against each other and candidates are competing but with different subjects, there is always difficulty in taking into account the fact that the candidates may be faced with papers of unequal difficulty, which are subsequently marked to different standards. Double markers consistently differ by 10 or even 20 per cent. It would appear that a standard method of marking ought to be put forward with sufficient authority to ensure general adoption and capable of eliminating the two difficulties mentioned, viz. variation in stiffness of papers as far as the candidates are concerned, and variation in the standard of marking. The scheme whereby the marks are altered by a factor which brings as many above the 50 per cent line as there are below and thereby unifies the standard of stiffness and of the marking before the papers are weighted or the class percentages are declared, has much to recommend it, and the author's views on this matter would be of value.

Logarithmic paper has long been in use by acoustic engineers to represent the responses of parts of, and complete, sound-reproducing systems, as it is found that departures from ideal criteria in sound-reproduction are more correctly represented by a logarithmic scale of frequency and logarithmic scales of power or amplitude. Response curves so drawn give approximately the right weighting of changes of frequency and power-level on the ear.

AUTHOR'S reply. I have no personal experience in the marking of examination papers but I believe that it is now not unusual for papers to be marked in such a fashion that about forty per cent of the candidates score between forty and sixty marks out of a hundred and that the frequency-distribution of marks is substantially normal. An examiner of experience should be able to set a paper and prepare a schedule of marks so as to secure such a distribution. A chief examiner must, of course, standardize the work of assistant examiners marking the same paper.

In a paper read last September before a joint session of Sections J and L of the British Association, Prof. Drever pointed out that an examination paper may be differently assessed not only by different examiners but also by the same examiner at different times.

THE BAND SPECTRUM OF BARIUM OXIDE

BY P. C. MAHANTI, M.Sc.

*Communicated by Prof. P. N. Ghosh, July 3, 1933, and in revised form
September 5, 1933. Read November 3, 1933.*

ABSTRACT. New measurements of the bands of barium oxide have been made from moderate-dispersion and high-dispersion spectrograms. The band-head data of the early investigations have been extended in the red region as far as $\lambda 8000$. The bands lying between $\lambda 8000$ – $\lambda 4300$ have been assigned to a single system. The equation representing the wave-numbers of band-heads is

$$\nu = 16815.89 + \{495.36 (v' + \frac{1}{2}) - 1.12 (v' + \frac{1}{2})^2\} \\ - \{671.48 (v'' + \frac{1}{2}) - 2.20 (v'' + \frac{1}{2})^2\}.$$

The bands (0, 3), (0, 2), (1, 2), (1, 1) and (2, 1) have been analysed. Their rotational structure reveals that the band system is due to a $^1\Sigma \rightarrow ^1\Sigma$ transition. The following rotational constants have been evaluated:

$$B_e' = 0.30995 \text{ cm}^{-1}$$

$$\alpha' = 0.0011$$

$$D_e' = -0.483 \times 10^{-8}$$

$$\beta' = 0.24 \times 10^{-8}$$

$$r_e' = 1.938 \times 10^{-8} \text{ cm.}$$

$$I_e' = 89.44 \times 10^{-40} \text{ gm. cm}^2$$

$$B_e'' = 0.36440 \text{ cm}^{-1}$$

$$\alpha'' = 0.0016$$

$$D_e'' = -0.430 \times 10^{-8}$$

$$\beta'' = -1.2 \times 10^{-8}$$

$$r_e'' = 1.787 \times 10^{-8} \text{ cm.}$$

$$I_e'' = 76.04 \times 10^{-40} \text{ gm. cm}^2$$

§ 1. INTRODUCTION

WHEN barium salts are introduced into a carbon arc in air, the spectrum shows a large number of bands consisting of several sequences which degrade towards longer wave-lengths and extend from the infra-red to the ultra-violet regions. In Kayser's *Handbuch der Spektroskopie*, volumes 5 and 7, one finds a record of the bands in the visible region as found by the early investigators when different compounds of barium were subjected to a variety of conditions of excitation, but there had been a great deal of speculation about the identity of the emitter. A systematic investigation of the spectra of barium halides in oxy-coal gas flame was conducted by Olmsted⁽¹⁾. He measured the bands in the region $\lambda 5865$ – $\lambda 3810$ and classified them into two groups. The group of narrow bands occupying the region $\lambda 4890$ – $\lambda 4850$ was attributed to the oxide while the second group, consisting of the remaining bands, was associated with the metal. This view was later supported by Börsch⁽²⁾, who extended the measurements of Olmsted in the red region up to $\lambda 7100$. But it was in conflict with the observations of Hartley⁽³⁾, who noticed that the bands of the second group would appear only when the metal was just beginning the process of oxidation, and was thus led to

believe that they are due to the oxide. Eder and Valenta⁽⁴⁾ were also of the same opinion and measured the band-heads as far as λ 3345. But it was Harnack⁽⁵⁾ who definitely settled the identity of their emitter. He extended the measurements of Eder and Valenta further in the ultra-violet up to λ 2300, and observed that these bands disappeared in an atmosphere of hydrogen and that the presence of oxygen was essential for their production. Their rotational analysis reveals that they are due to a $^1\Sigma \rightarrow ^1\Sigma$ transition. The odd multiplicity requires that the emitting molecule must have an even number of electrons. This definitely excludes the ionized-oxide molecule as the probable emitter, and the only possible conclusion is that the actual emitter of the bands is the neutral BaO molecule.

The first attempt to make a vibrational quantum analysis of the bands of barium oxide was made by Mecke and Guillery⁽⁶⁾ in 1927. They used, however, the older data, which are not in sufficiently close agreement with one another, as has been remarked by Kayser. Since then no further work has been done on these bands.

In the present investigation, the spectrum has been photographed under different dispersions and the measurements of band-heads extended in the region of the longer wave-lengths as far as λ 8000. Even with moderate dispersion the bands are partially resolved. In fact, their line structure was observed by several early investigators.

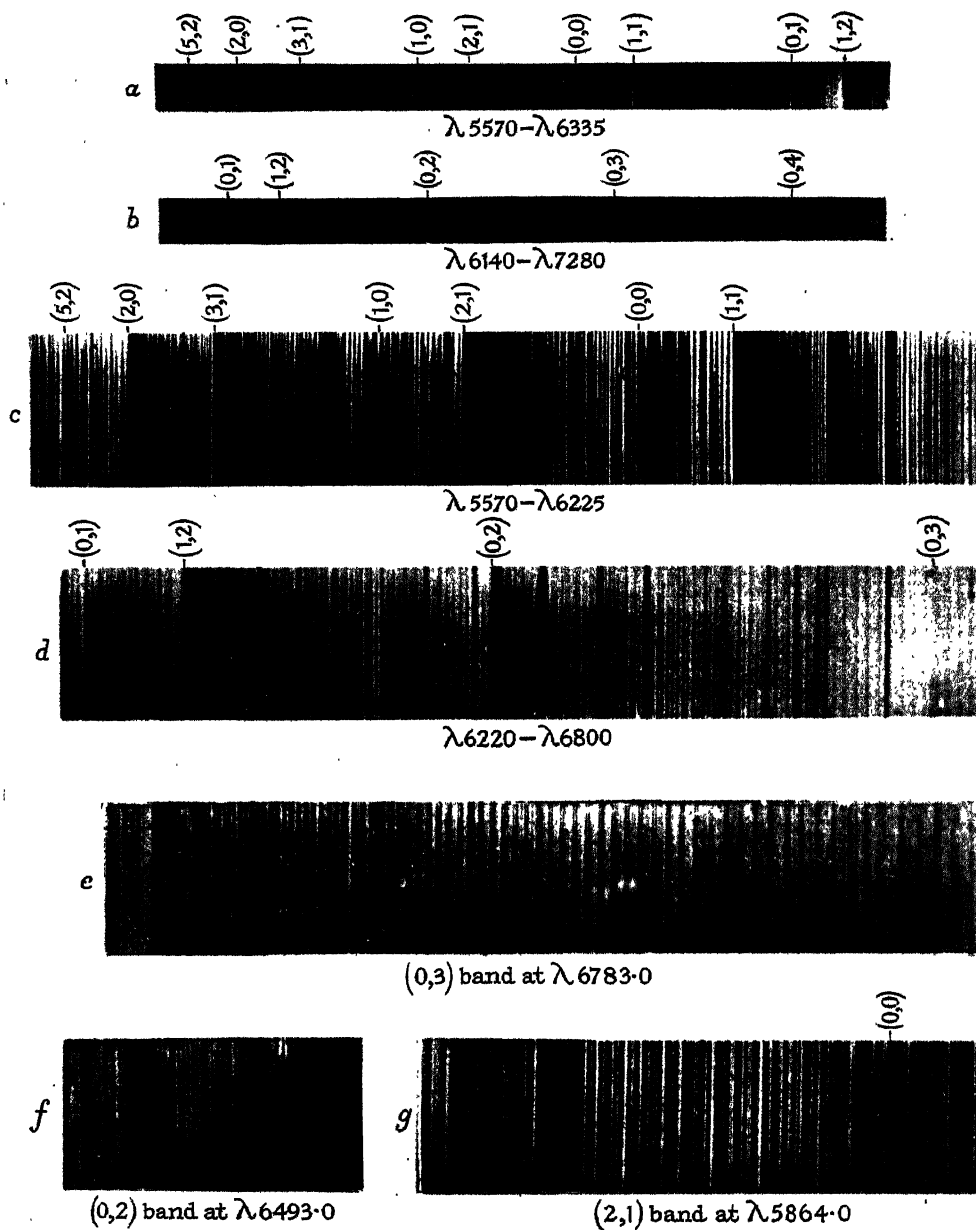
This paper has two objects. The first is to make a vibrational quantum analysis of the bands, based upon new measurements. It has been found that the bands between λ 8000– λ 4300 form a single system*. The second is to obtain the fine-structure analysis of this system.

§ 2. EXPERIMENTAL

In the present investigation the source employed is the flame surrounding a carbon arc with either BaCl_2 or $\text{Ba}(\text{NO}_3)_2$ in the lower (+) carbon, carrying a current of about eight amperes from 220-volt d.c. mains.

For a preliminary survey, spectrograms were taken with the Hilger Littrow-mounted E 1 quartz prism spectrograph in the region λ 7500– λ 2200. With Ilford Special Rapid Panchromatic plates, an exposure of about fifteen minutes was sufficient to get the bands strongly developed between λ 6800– λ 4300. Longer exposures were necessary to extend them on both ends. The extension of the bands in the red region was therefore taken up with the help of a Hilger E 52 glass prism spectrograph by using plates sensitized with pinacyanol and with rubro-cyanine

* A preliminary note about this spectrum was published in *Nature*, 181, 402 (1933), in which the bands were attributed to two systems, but there were a few fairly strong bands which could not be fitted into either of them. It was only on longer exposure that the nature of the rather faint band which forms the (0, 0) of the present system was disclosed, leading to the analysis into a single system which now includes all the observed bands. The intensity-distribution of the bands falls on a wide Condon parabola accounting for the weakness of the (0, 0) head. The result of the rotational analysis also supports this arrangement. The present paper, therefore, supersedes the above-mentioned note.



BaO bands; *a*, *b*, Hilger E 52 glass spectrograph; *c*, *d*, 6-ft. grating, first order; *e*, *f*, *g*, 15-ft. grating, first order.

as well as Ilford Infra-red-sensitive and Kodak Kryptocyanine plates. Bands were present as far as λ 8400, which is the maximum limit of sensitivity that can be obtained ordinarily with these plates. The heads are single and fairly sharp except where overlapping is great. But the bands below λ 4300, besides being superposed upon the violet CN bands and the OH bands, were found to be very weakly developed.

For measurements of band-heads, besides the quartz and the glass prism spectrograms photographs of the bands in the region λ 6900– λ 4800 were taken in the first order of a 6-ft. Rowland concave grating set up in a Paschen mounting and having a dispersion of about 8.9 Å./mm. A part of the spectrum under different dispersions is reproduced in the plate.

For measurements of structure lines, spectrograms were taken in the first and second orders of a 15-ft. concave grating set up in a similar mounting. The dispersion is about 1.8 Å./mm. in the second order. There is a complete resolution except for a few lines near the heads of the bands. For each band analysed the lines were measured at least twice on different spectrograms. The measurements of individual lines are considered to be accurate to within 0.05 cm.⁻¹

A Gaertner comparator was used for measurements. For standards of comparison, Pfund iron arc lines and neon lines were employed. In some regions, barium arc lines were also used. Precise measurements of band-heads lying between λ 8400 and λ 8000, and those below λ 4300, could not be made owing to the low intensity.

The measurements on different spectrograms revealed that practically all the band-heads (with the exception of a few weaker ones) that have been measured by the early investigators between λ 7100– λ 4300 have come out in the present investigation. Some of the weaker bands, especially those of Börsch in the red region, were found to be mere condensations of structure lines presenting the appearance of a head. The data of Olmsted and of Börsch appeared, however, to be more in agreement with the present values than those of Eder and Valenta.

§ 3. VIBRATIONAL ANALYSIS

The wave-length and wave-number data of band-heads together with the assignment of their vibrational quantum numbers are given in table 1. The relative photographic intensity data of the bands have been taken from those given by Olmsted and by Börsch. In cases where new band-heads have been measured, their intensities have been visually estimated in comparison with those of others. These intensity data are enclosed in brackets.

The equation representing the wave-number of band-heads is

$$\begin{aligned} \nu = 16815.89 + \{495.36 (v' + \frac{1}{2}) - 1.12 (v' + \frac{1}{2})^2\} \\ - \{671.48 (v'' + \frac{1}{2}) - 2.20 (v'' + \frac{1}{2})^2\} \quad \dots\dots(1). \end{aligned}$$

It may here be noted that the bands measured by the early investigators below λ 4300 probably belong to a different system.

Table 1. New data and vibrational quantum analysis

v'	v''	λ_{air}	$\nu_{\text{vac.}}$	v'	v''	λ_{air}	$\nu_{\text{vac.}}$
1	7	7905.10 (1)	12646.6	8	4	5562.39 (1)	973.9
0	6	7815.20 (3)	792.1	4	1	5547.82 (3)	18020.1
2	7	7610.10 (1)	13136.8	7	3	5509.73 (3)	144.7
1	6	7523.49 (2)	288.0	3	0	5492.69 (10)	201.0
0	5	7440.42 (4)	436.4	10	5	5470.50 (1)	274.8
3	7	7336.87 (1)	626.0	6	2	5454.61 (3)	328.0
2	6	7254.70 (2)	780.4	9	4	5419.77 (2)	445.9
1	5	7176.60 (3)	930.2	5	1	5402.68 (2)	504.2
0	4	7097.41 (5)	14085.8	8	3	5366.65 (2)	628.4
3	6	7007.15 (1)	267.2	4	0	5349.67 (8)	687.6
2	5	6931.43 (2)	423.1	7	2	5315.85 (1)	806.4
1	4	6857.22 (2)	579.2	6	1	5265.16 (1)	987.5
0	3	6782.79 (8)	739.1	9	3	5233.42 (1)	19102.7
3	5	6704.50 (2)	911.2	5	0	5214.68 (7)	171.3
2	4	6633.48 (2)	15070.9	8	2	5185.02 (1)	281.0
1	3	6563.20 (3)	232.3	7	1	5135.00 (1)	468.8
0	2	6493.09 (9)	396.7	10	3	5106.78 (1)	576.4
3	4	6423.12 (4)	564.5	6	0	5086.66 (6)	653.8
2	3	6358.05 (3)	723.8	9	2	5059.96 (1)	757.5
1	2	6291.01 (8)	891.3	8	1	5012.45 (2)	944.8
0	1	6224.66 (6)	16060.7	11	3	4988.06 (1)	20042.3
7	6	6169.58 (3)	204.1	7	0	4965.45 (3)	133.6
3	3	6165.11 (6)	215.8	10	2	4941.73 (2)	230.2
10	8	6116.20 (2)	345.2	9	1	4896.53 (2)	417.0
6	5	6111.00 (2)	359.4	12	3	4873.80 (4)	512.2
2	2	6102.32 (5)	382.7	8	0	4850.57 (6)	610.4
1	1	6039.64 (9)	552.7	11	2	4830.02 (2)	698.1
8	6	5996.60 (1)	671.5	10	1	4784.15 (4)	896.5
4	3	5984.86 (4)	704.2	13	3	4765.70 (2)	977.3
0	0	5976.28 (3)	728.1	9	0	4740.98 (4)	21086.8
7	5	5933.74 (1)	848.1	12	2	4722.73 (3)	168.3
3	2	5925.13 (2)	872.5	11	1	4680.27 (5)	360.3
10	7	5886.90 (4)	982.2	14	3	4663.50 (3)	437.1
6	4	5875.29 (2)	17015.7	10	0	4636.79 (4)	560.7
2	1	5864.51 (10)	047.0	13	2	4621.09 (4)	633.9
13	9	5839.98 (1)	118.6	12	1	4579.42 (4)	830.7
9	6	5829.20 (2)	150.3	11	0	4537.77 (2)	22030.0
5	3	5817.57 (2)	184.4	14	2	4524.01 (4)	098.1
1	0	5805.15 (6)	221.3	13	1	4483.80 (3)	296.3
8	5	5770.07 (3)	325.9	12	0	4442.61 (1)	503.0
4	2	5758.39 (3)	361.2	15	2	4430.60 (3)	564.0
7	4	5713.68 (3)	497.0	14	1	4391.26 (1)	766.1
3	1	5700.99 (8)	535.9	17	3	4381.20 (3)	818.4
10	6	5672.91 (4)	622.8	13	0	4353.90 (1)	961.5
6	3	5659.00 (2)	666.1	16	2	4343.30 (2)	23017.5
2	0	5644.13 (9)	712.7	15	1	4304.22 (1)	226.5
9	5	5615.42 (1)	803.1	14	0	4268.85 (2)	421.4
5	2	5602.37 (4)	844.7				

§ 4. ROTATIONAL ANALYSIS

The bands are of the simple two-branch type originating from a $^1\Sigma \rightarrow ^1\Sigma$ transition. Except for the (0, 2) band, the lines of the two branches form close doublets which coalesce into single lines as they approach the head; see (e) and (g) in the plate. In the (0, 2) band, apparently there is a single series of lines proceeding from the head. This is due to the superposition of the *R*-branch lines returning from

the head upon those of the same series proceeding towards the head from the origin as well as upon the lines of the *P*-branch as they run away from the origin; see (*f*) in the plate. Owing to high-temperature excitation of the bands, the series are long. No evidence was found of a *Q* branch, although a systematic search was made in every band for *Q* lines of low intensity. There is no sign of splitting into finer components even for last noticeable lines on the plates, and only a single line, *P*(0), is missing.

By definition,

$$R(K) = T'(K+1) - T''(K) \quad \text{.....(2),}$$

$$P(K) = T'(K-1) - T''(K) \quad \text{.....(3),}$$

so that

$$\Delta_2 T'(K) = R(K) - P(K) \quad \text{.....(4),}$$

$$\Delta_2 T''(K) = R(K-1) - P(K+1) \quad \text{.....(5).}$$

According to the combination principle, all bands having the same upper vibrational state should yield sets of values of $\Delta_2 T'(K)$ which are numerically identical; and similarly all bands having the same lower vibrational state should give identical sets of values of $\Delta_2 T''(K)$.

The wave-numbers of the lines together with their quantum assignments for each of the bands analysed as well as the values of $\Delta_2 T'(K)$ and $\Delta_2 T''(K)$ are given in tables 2 to 6.

The next step was to calculate the rotational constants of the molecule from the combination differences. Since the rotational energy of a molecule in a $^1\Sigma$ state is $T(K)$, where

$$T(K) = B_v K(K+1) + D_v K^2(K+1)^2 + \dots,$$

the combination differences can be expressed thus:

$$\begin{aligned} \Delta_2 T(K) &= T(K+1) - T(K-1) \\ &= 4B_v(K+\frac{1}{2}) + 8D_v(K+\frac{1}{2})^3 + \dots \end{aligned} \quad \text{.....(6),}$$

where terms small in comparison with $8D_v(K+\frac{1}{2})^3$ are dropped. Both B_v and D_v depend upon v according to the relations

$$\begin{aligned} B_v &= B_e - \alpha(v + \frac{1}{2}) \\ &= B_0 - \alpha v \end{aligned} \quad \text{.....(7),}$$

and

$$\begin{aligned} D_v &= D_e + \beta(v + \frac{1}{2}) \\ &= D_0 + \beta v \end{aligned} \quad \text{.....(8).}$$

Here B_e and D_e are the extrapolated values of B_v and D_v corresponding to the non-vibrating molecule.

The mean values of the combination differences $\Delta_2 T(K)$ have been taken in cases where there was more than one datum available for a particular pair of rotational levels. For each vibrational level, the values of $\Delta_2 T(K)$ were plotted against K . It was found that the points lay very approximately on a straight line, so that terms of higher power than the third need not be considered and the term involving the third power is itself very small. The slope of this line in each case gave also a good approximation to the value of $4B_v$.

Table 2. Structure of the (0, 3) band

K	$R(K)$	$P(K)$	$\Delta_2 T'(K)$ ($v' = 0$)	$\Delta_2 T''(K)$ ($v'' = 3$)	K	$R(K)$	$P(K)$	$\Delta_2 T'(K)$ ($v' = 0$)	$\Delta_2 T''(K)$ ($v'' = 3$)
0	—	—	—	—	51	36.38	73.14	63.24	73.51
1	—	14736.42	—	—	52	31.82	67.39	64.43	—
2	—	35.48	—	—	53	27.10	—	—	76.31
3	—	34.51	—	—	54	22.32	55.51	66.81	77.69
4	—	33.47	—	—	55	17.46	49.41	68.05	79.11
5	—	32.38	—	—	56	12.46	43.21	69.25	80.46
6	14739.13	31.10	8.03	—	57	07.42	37.00	70.42	81.87
7	39.13	29.82	9.31	10.79	58	02.22	30.59	71.63	83.27
8	38.90	28.34	10.56	12.22	59	596.95	24.15	72.80	84.69
9	38.68	26.91	11.77	13.68	60	91.54	17.53	74.02	86.10
10	38.26	25.22	13.04	15.09	61	86.05	10.85	75.20	87.46
11	37.85	23.59	14.26	16.53	62	80.47	04.07	76.40	88.86
12	37.24	21.73	15.51	17.97	63	74.78	497.19	77.59	90.28
13	36.61	19.88	16.73	19.39	64	14568.96	14490.19	78.77	91.64
14	35.76	17.85	17.91	20.80	65	63.10	83.14	79.96	93.01
15	34.92	15.81	19.11	22.20	66	57.10	75.95	81.15	94.40
16	33.90	13.56	20.34	23.64	67	51.02	68.70	82.32	95.79
17	32.86	11.28	21.58	25.11	68	44.86	61.31	83.55	97.18
18	31.60	08.79	22.81	26.51	69	38.53	53.84	84.69	98.64
19	14730.38	14706.35	24.03	27.95	70	32.13	46.22	85.91	99.97
20	28.93	03.65	25.28	29.35	71	25.65	38.56	87.09	101.34
21	27.54	01.03	26.51	30.77	72	19.09	30.79	88.30	102.69
22	25.91	698.16	27.75	32.20	73	12.40	22.96	89.44	104.09
23	24.31	95.33	28.98	33.67	74	05.60	15.00	90.60	105.48
24	22.46	92.24	30.22	35.09	75	498.70	06.92	91.78	106.86
25	20.64	89.22	31.42	36.50	76	91.70	398.74	92.96	108.23
26	18.60	85.96	32.64	37.94	77	84.61	90.47	94.14	109.59
27	16.57	82.70	33.87	39.39	78	77.39	82.11	95.28	111.06
28	14.32	79.21	35.11	40.85	79	70.04	73.55	96.49	112.37
29	12.06	75.72	36.34	42.22	80	62.65	65.02	97.63	113.65
30	09.64	72.10	37.54	43.62	81	55.16	56.39	98.77	115.12
31	07.19	68.44	38.75	45.05	82	47.54	47.53	100.01	116.52
32	04.58	64.59	39.99	46.47	83	39.81	38.64	101.17	117.84
33	01.96	60.72	41.24	47.91	84	32.00	29.70	102.30	119.20
34	699.15	56.67	42.48	49.41	85	24.11	20.61	103.50	120.59
35	96.28	52.55	43.73	50.83	86	16.10	11.41	104.69	122.00
36	93.26	48.32	44.94	52.29	87	07.99	02.11	105.88	123.29
37	14690.17	14643.99	46.18	53.71	88	399.80	292.81	106.99	124.64
38	86.95	39.55	47.40	55.12	89	91.51	83.35	108.16	—
39	83.67	35.05	48.62	56.55	90	83.12	—	—	—
40	80.26	30.40	49.86	57.98	91	14374.60	—	—	—
41	76.79	25.69	51.10	59.38	92	66.01	—	—	—
42	73.20	20.88	52.32	60.80	93	57.32	—	—	—
43	69.52	15.99	53.53	62.15	94	48.48	—	—	—
44	65.81	11.05	54.76	63.57	95	39.63	—	—	—
45	61.90	05.95	55.95	65.08	96	30.63	—	—	—
46	57.90	00.73	57.17	66.49	97	14321.55	—	—	—
47	53.80	595.41	58.39	67.87	98	12.31	—	—	—
48	49.63	90.03	59.60	69.33	99	03.01	—	—	—
49	45.27	84.47	60.80	70.75	100	293.63	—	—	—
50	40.90	78.88	62.02	72.13	101	84.11	—	—	—

These figures for B_v were then used to calculate approximately the values of D_v from several observed values of $\Delta_2 T'(K)$. Then by successive approximation and repeated trials values were finally assigned to B_v and D_v . The values of B_v thus found showed a linear variation according to equation (7). The values of D_v were

Table 3. Structure of the (0, 2) band

<i>K</i>	<i>R</i> (<i>K</i>)	<i>P</i> (<i>K</i>)	$\Delta_2 T'(K)$ (<i>v'</i> = 0)	$\Delta_2 T''(K)$ (<i>v''</i> = 2)	<i>K</i>	<i>R</i> (<i>K</i>)	<i>P</i> (<i>K</i>)	$\Delta_2 T'(K)$ (<i>v'</i> = 0)	$\Delta_2 T''(K)$ (<i>v''</i> = 2)
0	15395.10				37	45.65	299.45	46.20	53.89
1	95.65	15393.78	1.87	2.15	38	42.39	94.96	47.43	55.28
2	96.05	92.95	3.10	3.60	39	39.03	90.37	48.66	56.69
3	96.41	92.05	4.36	5.05	40	35.57	85.70	49.87	58.12
4	96.60	91.00	5.60	6.50	41	31.99	80.91	51.08	59.59
5	96.74	89.91	6.83	—	42	28.32	75.98	52.34	61.03
6	96.74	—	—	—	43	24.52	70.96	53.56	62.51
7	96.60	—	—	10.83	44	20.58	65.81	54.77	63.91
8	96.41	85.91	10.50	—	45	—	60.61	—	65.28
9	96.05	—	—	—	46	12.46	55.30	57.16	—
10	95.65	—	—	15.20	47	08.21	49.84	58.37	68.18
11	95.10	80.85	14.25	16.60	48	03.90	44.28	59.62	69.58
12	94.51	79.05	15.46	18.02	49	299.45	38.63	60.82	70.96
13	93.78	77.08	16.70	19.48	50	94.96	32.94	62.02	72.31
14	92.95	75.03	17.92	20.91	51	90.37	27.14	63.23	73.70
15	92.05	72.87	19.18	22.29	52	15285.70	15221.26	64.44	—
16	15391.00	15370.66	20.34	23.73	53	80.91	—	—	—
17	89.91	68.32	21.59	25.14	54	75.98	—	—	—
18	—	65.86	—	26.60	55	70.96	—	—	—
19	—	63.31	—	—	56	65.81	—	—	—
20	85.91	60.62	25.29	—	57	60.61	—	—	—
21	—	57.81	—	30.98	58	55.30	—	—	—
22	—	54.93	—	—	59	49.84	—	—	—
23	80.85	51.91	28.94	—	60	44.28	—	—	—
24	79.05	48.85	30.20	35.20	61	38.63	—	—	—
25	77.08	45.65	31.43	36.66	62	32.94	—	—	—
26	75.03	42.39	32.64	38.05	63	27.14	—	—	—
27	72.87	39.03	33.84	39.46	64	21.26	—	—	—
28	70.66	35.57	35.09	40.88	65	14.98	—	—	—
29	68.32	31.99	36.33	42.34	66	08.87	—	—	—
30	65.86	28.32	37.54	43.80	67	02.62	—	—	—
31	15363.31	15324.52	38.79	45.28	68	196.20	—	—	—
32	60.62	20.58	40.04	—	69	89.62	—	—	—
33	57.81	—	—	48.16	70	83.20	—	—	—
34	54.93	12.46	42.47	49.60	71	76.43	—	—	—
35	51.91	08.21	43.70	51.03	72	69.63	—	—	—
36	48.85	03.90	44.95	52.46					

found to be practically constant, so that β is negligibly small. Its value was, however, calculated from the theoretical formula

$$\beta = \frac{\alpha^2}{6\omega_e} + \frac{20\alpha B_e^2 - 32x_e B_e^3}{\omega_e^2} \quad \text{.....(9).}$$

The following constants were thus evaluated:

$$B_e' = 0.30995 \text{ cm}^{-1}$$

$$B_0' = 0.3094$$

$$B_1' = 0.3083$$

$$B_2' = 0.3072$$

$$\alpha' = 0.0011$$

$$D_e' = -0.483 \times 10^{-6}$$

$$\beta' \text{ (calculated)} = 0.24 \times 10^{-9}$$

$$r_e' = 1.938 \times 10^{-8} \text{ cm.}$$

$$I_e' = 89.44 \times 10^{-40} \text{ gm. cm}^2$$

$$B_e'' = 0.36440 \text{ cm}^{-1}$$

$$B_1'' = 0.3620$$

$$B_2'' = 0.3604$$

$$B_3'' = 0.3588$$

$$\alpha'' = 0.0016$$

$$D_e'' = -0.430 \times 10^{-6}$$

$$\beta'' \text{ (calculated)} = -1.2 \times 10^{-9}$$

$$r_e'' = 1.787 \times 10^{-8} \text{ cm.}$$

$$I_e'' = 76.04 \times 10^{-40} \text{ gm. cm}^2$$

Table 4. Structure of the (1, 2) band

K	$R(K)$	$P(K)$	$\Delta_2 T'(K)$ ($v' = 1$)	$\Delta_2 T''(K)$ ($v'' = 2$)	K	$R(K)$	$P(K)$	$\Delta_2 T'(K)$ ($v' = 1$)	$\Delta_2 T''(K)$ ($v'' = 2$)
0	—	—	—	—	30	15859.40	15822.00	37.40	43.88
1	—	—	—	—	31	56.71	18.09	38.62	45.31
2	—	—	—	—	32	53.92	14.09	39.83	46.72
3	—	—	—	—	33	51.05	09.99	41.06	48.15
4	—	15886.04	—	—	34	48.06	05.77	42.29	49.61
5	—	84.70	—	—	35	45.00	01.44	43.56	51.01
6	15891.31	83.31	8.00	—	36	41.86	797.05	44.81	52.47
7	91.11	81.90	9.21	10.80	37	38.54	92.53	46.01	53.94
8	90.91	80.51	10.40	12.26	38	35.13	87.92	47.21	55.31
9	90.51	78.85	11.66	13.73	39	31.62	83.23	48.39	56.76
10	90.10	77.18	12.92	15.14	40	28.01	78.37	49.64	58.12
11	89.60	75.37	14.23	16.60	41	24.35	73.50	50.85	59.62
12	88.92	73.50	15.42	18.04	42	20.45	68.39	52.06	—
13	88.21	71.56	16.65	19.43	43	16.52	—	—	62.47
14	87.38	69.49	17.89	20.91	44	12.57	57.98	54.59	63.90
15	86.39	67.30	19.09	22.29	45	08.39	52.62	55.77	65.34
16	85.40	65.09	20.31	23.72	46	04.27	47.23	57.04	66.74
17	84.19	62.67	21.52	25.17	47	799.92	41.65	58.27	—
18	82.96	60.23	22.73	26.60	48	95.53	—	—	—
19	81.57	57.59	23.98	28.11	49	90.96	—	—	—
20	80.06	54.85	25.21	29.57	50	86.32	—	—	—
21	78.42	52.00	26.42	30.97	51	81.56	—	—	—
22	76.75	49.09	27.66	32.39	52	76.66	—	—	—
23	74.91	46.03	28.88	33.84	53	71.60	—	—	—
24	73.02	42.91	30.11	35.21	54	66.43	—	—	—
25	71.05	39.70	31.35	36.63	55	61.11	—	—	—
26	68.96	36.39	32.57	38.07	56	55.70	—	—	—
27	66.77	32.98	33.79	39.57	57	50.21	—	—	—
28	64.41	29.39	35.02	40.99	58	44.58	—	—	—
29	61.97	25.78	36.19	42.41					

The difference between the observed and calculated values of $\Delta_2 T'(K)$ and $\Delta_2 T''(K)$ from equation (6) is not of any sensible magnitude even for large quantum numbers. This indicates that the coupling conforms to Hund's case (b) as classified by Mulliken⁽⁷⁾.

A check on the correctness of the analysis is afforded by the theoretical relation

$$\omega_e^2 = -4B_e^3/D_e \quad \text{.....(10).}$$

On substitution of the proper values of B_e and D_e , it is found that $\omega_e' = 496 \text{ cm}^{-1}$ and $\omega_e'' = 671 \text{ cm}^{-1}$. These values are in sufficiently close agreement with those obtained from the vibrational analysis of the bands.

A further check is afforded by Birge's rule⁽⁸⁾:

$$2x_e B_e / \alpha = 1.4 \pm 0.2 \quad \text{.....(11).}$$

For these bands substitution of the proper values shows that

$$2x_e' B_e' / \alpha' = 1.27 \text{ and } 2x_e'' B_e'' / \alpha'' = 1.49 \quad \text{.....(12).}$$

A third check is obtained from the approximate relation between ω_e and r_e as given by Morse⁽⁹⁾:

$$\omega_e r_e^3 = \text{constant} \quad \text{.....(13).}$$

Table 5. Structure of the (1, 1) band

K	$R(K)$	$P(K)$	$\Delta_2 T'(K)$ ($v' = 1$)	$\Delta_2 T''(K)$ ($v'' = 1$)	K	$R(K)$	$P(K)$	$\Delta_2 T'(K)$ ($v' = 1$)	$\Delta_2 T''(K)$ ($v'' = 1$)
0	—	—	—	—	30	16519.42	16481.97	37.45	44.09
1	—	—	—	—	31	16.69	77.98	38.71	45.54
2	—	—	—	—	32	13.88	73.88	40.00	46.96
3	—	—	—	—	33	10.93	69.73	41.20	48.39
4	—	—	—	—	34	07.88	65.49	42.39	49.80
5	—	16546.08	—	—	35	04.72	61.13	43.59	51.30
6	16552.71	44.71	8.00	—	36	01.42	56.58	44.84	52.80
7	52.51	43.31	9.20	10.85	37	497.99	51.92	46.07	54.21
8	52.30	41.86	10.44	12.29	38	94.54	47.21	47.33	55.62
9	51.91	40.22	11.69	13.75	39	90.89	42.37	48.52	57.12
10	51.48	38.55	12.93	15.22	40	—	37.42	—	58.50
11	50.87	36.69	14.18	16.73	41	83.41	32.39	51.02	—
12	50.16	34.75	15.41	18.12	42	79.50	27.26	52.24	61.41
13	49.39	32.75	16.64	19.57	43	75.48	22.00	53.48	62.94
14	48.46	30.59	17.87	20.99	44	71.27	16.56	54.71	64.40
15	47.47	28.40	19.07	22.35	45	66.93	11.08	55.84	65.73
16	46.41	26.11	20.30	23.79	46	62.59	05.54	57.05	—
17	45.23	23.68	21.55	25.27	47	58.26	—	—	—
18	43.91	21.14	22.77	26.74	48	53.71	—	—	—
19	42.49	18.49	24.00	28.17	49	48.94	—	—	—
20	40.96	15.74	25.22	29.65	50	44.07	—	—	—
21	39.29	12.84	26.45	31.12	51	39.18	—	—	—
22	37.51	09.84	27.67	32.55	52	34.18	—	—	—
23	35.65	06.74	28.91	33.99	53	29.05	—	—	—
24	33.65	03.52	30.13	35.45	54	23.70	—	—	—
25	31.55	00.20	31.35	36.91	55	18.25	—	—	—
26	29.31	496.74	32.57	38.35	56	12.70	—	—	—
27	27.01	93.20	33.81	—	57	06.94	—	—	—
28	24.61	—	—	41.15	58	01.10	—	—	—
29	22.07	85.86	36.21	42.64					

It has been well established that this constant has a value equal to $3000 \times 10^{-24} \text{ cm}^2$ in the cases of diatomic molecules composed of atoms of nearly equal mass. But if the masses of the atoms are unequal, as in the present case, the value of this constant should be greater than $3000 \times 10^{-24} \text{ cm}^2$. This condition is satisfied since we have

$$\omega_e' r_e'^3 = 3605 \times 10^{-24} \text{ cm}^2 \text{ and } \omega_e'' r_e''^3 = 3830 \times 10^{-24} \text{ cm}^2 \quad \dots\dots(14).$$

The heats of dissociation for the upper as well as for the lower states have been calculated from the expression

$$D = \omega_e^2 / 4x_e \omega_e \quad \dots\dots(15),$$

and are found to be 6.76 and 6.32 volts respectively.

From the relation

$$\nu_{(\text{atom})} + D' = D'' + \nu_{(\text{atom})} \quad \dots\dots(16),$$

$\nu_{(\text{atom})}$ is calculated to be 2.52 volts.

It may here be pointed out that Mulliken⁽¹⁰⁾ in discussing the constitution of BeO molecule has suggested its normal state to be derived from Be (¹S) + O (¹D) atoms. For the homologous molecule BaO, it may not be unjustifiable to suppose that if the lower state of the observed band system is its normal state it will dissociate into B (¹S) and O (¹D) atoms, and in the upper state it will dissociate into

Table 6. Structure of the (2, 1) band

K	$R(K)$	$P(K)$	$\Delta_2 T'(K)$ ($v' = 2$)	$\Delta_2 T''(K)$ ($v'' = 1$)	K	$R(K)$	$P(K)$	$\Delta_2 T'(K)$ ($v' = 2$)	$\Delta_2 T''(K)$ ($v'' = 1$)
0	—	—	—	—	38	84.28	37.35	46.93	55.53
1	—	—	—	—	39	80.41	32.44	47.97	57.00
2	—	17043.49	—	—	40	76.58	27.28	49.30	—
3	—	42.51	—	—	41	—	—	—	59.84
4	—	41.40	—	—	42	68.47	16.71	51.76	—
5	17046.01	40.24	6.77	—	43	64.13	11.24	52.89	62.66
6	—	38.99	—	9.41	44	59.76	05.81	53.95	63.95
7	—	37.60	—	—	45	—	00.18	—	65.32
8	—	36.03	—	—	46	50.76	804.44	56.32	—
9	—	34.40	—	—	47	46.05	88.59	57.45	68.27
10	17045.32	32.43	12.89	—	48	41.28	82.49	58.79	69.75
11	44.71	30.63	14.08	16.69	49	36.40	76.30	60.10	71.13
12	43.93	28.63	15.30	18.11	50	31.35	70.15	61.20	72.56
13	43.00	26.60	16.40	19.56	51	26.22	63.84	62.38	74.00
14	41.92	24.37	17.55	20.98	52	20.98	57.35	63.63	75.43
15	40.79	22.02	18.77	22.42	53	15.62	50.79	64.83	76.89
16	39.51	19.50	20.01	23.87	54	10.19	44.09	66.10	78.23
17	38.15	16.92	21.23	25.28	55	04.64	37.39	67.25	79.69
18	36.70	14.23	22.47	26.73	56	898.98	30.50	68.48	81.13
19	35.19	11.42	23.77	28.18	57	93.19	23.51	69.68	82.57
20	33.59	08.52	25.07	29.65	58	16887.31	16816.41	70.90	84.05
21	31.79	05.54	26.29	31.14	59	81.24	09.14	72.10	85.46
22	29.88	02.45	27.43	32.55	60	75.16	01.85	73.31	86.89
23	27.85	16999.24	28.61	34.02	61	68.85	794.35	74.50	88.32
24	25.70	95.86	29.84	35.49	62	62.56	86.84	75.72	89.84
25	23.50	92.36	31.14	36.92	63	55.96	79.01	76.95	91.46
26	21.12	88.78	32.34	38.36	64	49.31	71.10	78.21	—
27	18.66	85.14	33.52	39.78	65	42.81	—	—	—
28	16.08	81.34	34.74	41.19	66	35.98	—	—	—
29	17013.47	16977.47	36.00	—	67	16829.12	—	—	—
30	10.69	—	—	44.04	68	22.07	—	—	—
31	07.77	69.43	38.34	45.49	69	15.08	—	—	—
32	04.76	65.20	39.56	46.97	70	07.90	—	—	—
33	01.58	60.80	40.78	—	71	00.64	—	—	—
34	16998.37	—	—	49.82	72	793.21	—	—	—
35	95.02	51.76	43.26	51.29	73	85.63	—	—	—
36	91.52	47.08	44.44	52.74	74	77.97	—	—	—
37	87.97	42.28	45.69	54.17	75	70.17	—	—	—

Ba ($1P^0$) and O ($1D$) atoms. Such an assumption finds a support from the fact that from the data of energy states published by Bacher and Goudsmit⁽¹¹⁾, the difference of energy values between a Ba atom in ($6s^2$) $1S$ state and that in a ($6s6p$) $1P^0$ excited state is 2.23 volts, differing by about 0.3 volt from that calculated from the present data. Such a discrepancy may well be expected in a calculation where the dissociation energies have been derived by long extrapolation.

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THE ACTION OF A TUNED RECTANGULAR FRAME AERIAL WHEN TRANSMITTING SHORT WAVES

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ABSTRACT. The work described in this communication is a continuation of a paper by one of us (L. S. P.) on the action of a tuned rectangular frame aerial when receiving short waves. The present development deals with the somewhat similar problem of the action of a tuned rectangular frame aerial when transmitting short waves. Experiments are described which show that a variation of the frame-dimensions affects both the frame current and the radiation, and that these quantities will only attain their maximum values if the frame-dimensions are suitably adjusted.

A theory is developed to account for the observed phenomena, and equations are obtained the solutions of which give approximately the necessary conditions for maximum frame current and maximum radiation.

§ 1. INTRODUCTION

IT has been known for some time that the action of a frame aerial when used with short waves comparable in length to the frame-dimensions is quite different from its action when used with long waves. In a recent investigation* one of us (L. S. P.) has shown that, when a tuned frame aerial comparable in dimensions to the wave-length is used for reception, the received current is very critically dependent on the frame-dimensions, and that by suitably varying the dimensions the current may be adjusted to a maximum. These facts were explained by taking into consideration the mutual action between the different limbs of the frame. Equations were developed which expressed the conditions for maximum frame current. These were eventually simplified to

$$\tan [a (1 + \cos \gamma) - \psi] = (a^2 - 1)/a \quad \dots\dots(1),$$

$$\tan [a' (1 + \sin \gamma) + \psi] = (a'^2 - 1)/a' \quad \dots\dots(2),$$

where $a = 2\pi W/\lambda$, $a' = 2\pi H/\lambda$, γ is the angle of incidence of the wave on the frame, and ψ is an arbitrary phase angle.

For convenience, this process of obtaining maximum frame current by the fulfilment of the above conditions has tentatively been called "formatization"† to distinguish it from the process of tuning, and the purpose of the present paper is to

* *Proc. R.S. A* 136, 193-209 (1932).

† *Loc. cit.* p. 208.

develop a similar theory of formatization of tuned rectangular frame aerals when used for transmission.

In a previous paper the electro-magnetic wave incident on the frame was considered to cause a frame current which can be resolved into an initial component due to the primary action of the wave, and a supplemental component due to the field of the current in the adjacent parts of the frame. It was then assumed that the condition for maximum frame current is that the initial and supplemental components shall be in phase*. It was thought that this assumption was justified provided that (i) the component currents are uniformly distributed and (ii) the amplitudes of the component currents are sensibly independent of the frame-dimensions.

The question of the resultant current-distribution has now been investigated† and it is found that the current-variation round a short-wave frame aerial depends on the ratio of the perimeter of the frame to the wave-length. Experiments show that the consequent lack of uniformity in the frame current does not vitiate the assumption that the frame current is a maximum when the supplemental and initial components are in phase. If we consider any infinitely small length of the wire, then the currents flowing in any such elemental length may be taken to be uniformly distributed throughout the length at any given instant, and the co-phasing of the supplemental and initial elemental currents leads to the same formatizing conditions as are given in equations (1) and (2) above, because the phase angles are independent of the current-amplitudes. It would therefore appear that the uniformity of the component currents throughout the whole length of any limb of the frame is not a necessary condition for the establishment of maximum frame current. The fact that the experimental points in figures 7, 8 and 13 lie close to the theoretical curves gives additional support to this conclusion.

The second assumption has been shown to be justified as long as the distances between adjacent limbs are not less than about 0.2λ ‡. With these assumptions, equations (1) and (2) were developed; they give the critical values of H/λ and W/λ for maximum current in a tuned rectangular frame receiving from a given source in a given direction determined by the value of γ . Conversely, from the reciprocity principle, a frame will transmit most effectively to the same source along the same path but in the reverse direction, when it is similarly proportioned and when the same currents circulate in it.

If, when the frame is used for transmission, the currents are to be produced in it not by a passing wave but by a local oscillator, then the optimum frame-dimensions for maximum current may not be the same as when the necessary energy is absorbed from a passing wave. Consequently, when the frame current produced by the local oscillator is a maximum, the frame-dimensions may not be correct for optimum radiation in the required direction; and vice versa, when the frame

* Palmer and Honeyball, *Proc. Inst. Rad. Eng.* 20, 1349 (1932).

† See pp. 76-84 of this volume.

‡ Palmer and Honeyball, *J. Inst. E.E.* 67, 1046 (1929), and Ratcliffe, Vedy and Wilkins, *ibid.* 70 522 (1932).

is correctly proportioned for maximum radiation, the current in it may not be a maximum.

In view of these considerations, it seems desirable to study first the variation, as the frame-dimensions are changed, of the frame current produced by a local oscillator and then to proceed to the more complicated conditions for maximum radiation.

Therefore, in the next section the conditions necessary for the production of maximum current in the transmitting frame will be considered, and afterwards the more complicated conditions for maximum radiation will be studied.

§ 2. THEORETICAL CONDITIONS FOR MAXIMUM FRAME CURRENT

Consider a rectangular frame directly coupled to, and actuated by, a local valve oscillator. The applied e.m.f., assumed constant, will generate a local current which will eventually affect all parts of the frame because they are influenced by the electromagnetic field set up, and also because they are metalically interconnected to form a closed circuit. Hence the current in any limb of the frame is the resultant of three components, namely (i) that produced directly by the transmitter, which we may call the *initial* current; (ii) that produced indirectly by waves travelling across the space between parallel adjacent wires, which, for convenience, we may call the *first supplemental* current; and (iii) that produced indirectly by waves travelling round the perimeter of the frame, which we may call the *second supplemental* current. Only the first two were considered in the previous papers.

Since the magnitude and the phase of the supplemental components are dependent on the frame-dimensions, it follows that the resultant current is also dependent on the frame-dimensions, and that by suitable variation of the dimensions the frame current can be adjusted to a maximum. In this section, the conditions necessary for the establishment of this maximum frame current, when the frame has already been tuned in the ordinary way, will be considered.

Since the amplitudes of the component currents are sensibly independent of the dimensions of the frame as long as these exceed 0.2λ , the condition for maximum frame current is that the current components shall be in phase. In order to develop the necessary equations, the phase of the supplemental components must be calculated.

First formatizing conditions. Consider the first supplemental current component due to the presence of the initial current in, say, an element of one of the horizontal limbs of the frame. Let the initial current be $I_0 \sin \omega t$ and let it be uniform throughout the element.

Then the electric moment is given by

$$- \int I_0 \sin \omega t dt = (I_0 \cos \omega t) / \omega.$$

This results in a field a distance H away such that the horizontal electric force is given by

$$\begin{aligned} E &= -AI_0 \left\{ \frac{1}{H^3} \cos(\omega t - a') + \frac{1}{vH^2} \frac{d}{dt} [\cos(\omega t - a')] + \frac{1}{v^2H} \frac{d^2}{dt^2} [\cos(\omega t - a')] \right\} \\ &= \frac{AI_0}{H^3} \sqrt{(a'^2 - 1)^2 + a'^2} \cdot \sin(\omega t - a' + \phi'), \end{aligned}$$

or

$$E_0 \sin (\omega t - a' + \phi'),$$

where $E_0 = \frac{AI_0}{H^3} \sqrt{\{(a'^2 - 1)^2 + a'^2\}}$ and $\tan \phi' = (a'^2 - 1)/a'$.

If the frame be tuned, the current produced by this e.m.f. will be in phase with it, and therefore the first supplemental current in one horizontal element will differ in phase from the initial current in the opposite element by

$$- a' + \phi'.$$

Hence, for the first supplemental current to be in phase with the initial current in the same element, the energy must be re-radiated from the opposite element. Consequently reinforcement will occur if

$$2(-a' + \phi') = 0 \text{ or } 2n\pi \quad \dots\dots(3),$$

where n is any integer.

A precisely similar argument shows that the condition for these two current components to be in phase in the vertical members of the frame is

$$2(-a + \phi) = 0 \text{ or } 2n\pi \quad \dots\dots(4),$$

where

$$\tan \phi = (a^2 - 1)/a.$$

These equations reduce to

$$(a^2 - 1)/a = \tan (n\pi + a) = \tan a \quad \dots\dots(5)$$

and

$$(a'^2 - 1)/a' = \tan (n\pi + a') = \tan a' \quad \dots\dots(6).$$

These transcendental equations have been solved by a graphical method and the solutions are

$$a = a' = 4.45, 7.70, \text{ etc.},$$

i.e.

$$W/\lambda = H/\lambda = 0.71, 1.20, \text{ etc.}$$

There is an ambiguity in these solutions, because equations (5) and (6) also represent the conditions for minimum frame current. Experiments show, however, that alternate solutions give maximum and minimum values respectively.

Thus we conclude that a frame of height 0.71λ and width 0.71λ will have an abnormally large current circulating round it when directly coupled to an oscillator. This result may be compared with that for maximum receiving current, namely, that when the frame-height was 0.71λ the optimum width was either 0.33λ or 0.85λ , and the frame was not square as in the present case.

Now the early experiments showed that if the critical width be altered, then a large current could still be maintained by suitably varying the height. This can be explained, as in the previous paper*, by extending the above reasoning as follows:

Suppose the frame-width be increased so that the phase angle between the component currents is not $2n\pi$ but $(2n\pi - 2\psi)$, say, then

$$2(-a + \phi) = 2n\pi - 2\psi \quad \dots\dots(7).$$

The new width may be considered to act as an added inductance producing the undesirable phase-lag ψ . If now the height be decreased just sufficiently to produce a phase lead of $(2n\pi + 2\psi)$ in the currents in the horizontal wires of the frame, then

* *Proc. R.S. A* 136, 196 (1932).

the effect on the frame current is similar to that of introducing a capacity of sufficient magnitude to compensate for the inductive effect of increasing the frame-width. Thus

$$2(-a' + \phi') = 2n\pi + 2\psi \quad \dots\dots(8).$$

Equations (7) and (8) reduce to

$$(a^2 - 1)/a = \tan(n\pi + a - \psi) = \tan(a - \psi) \quad \dots\dots(9)$$

and $(a'^2 - 1)/a' = \tan(n\pi + a' + \psi) = \tan(a' + \psi) \quad \dots\dots(10).$

The frame-dimensions (that is the value of H/λ and W/λ) for different values of ψ can be calculated from the above transcendental equations. This has been done by a graphical method and the relation between H/λ and W/λ is shown by the curve marked (a) in figure 1.

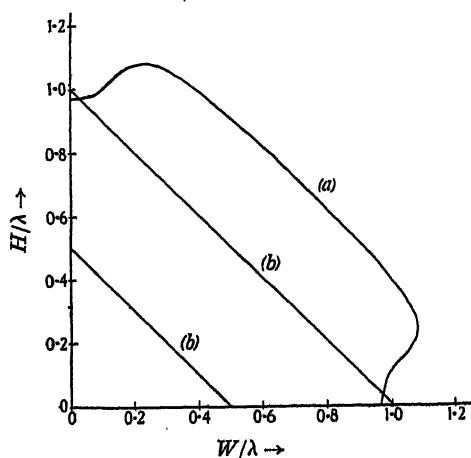


Figure 1.

Thus any point on this graph gives the frame-dimensions in terms of H/λ and W/λ for which the resultant current will be a maximum. For convenience these conditions will be called the *first formatizing conditions**.

In general, they will be quite different from those conditions necessary to make the second supplemental current be in phase with the initial current. Consequently, there will be a further set of conditions (conveniently referred to as the *second formatizing conditions*) depending on the critical dimension for the co-phasing of these two components. These conditions will now be considered.

Second formatizing conditions. In any element of the frame, let the initial current be $I_0 \sin \omega t$ (say): the second supplemental current will be that due to the return of the wave to the element under consideration after it has travelled round the frame. With a frame of negligible resistance the reduction in amplitude, as the wave travels round the frame, will be due mainly to the loss of energy by

* The same conditions may be deduced by considering the effect of an infinite number of re-radiations to and fro between opposite limbs of the frame.

radiation. It is shown below in §§ 4, 5 that for maximum current under these conditions the radiation is zero, and hence the resultant current will be given by

$$I_0 \sin \omega t + I_0 \sin (\omega t - 2\pi l/\lambda),$$

where l is the frame-perimeter and therefore equal to $2(H + W)$. The amplitude of the resultant current is $2I_0 \cos (\pi l/\lambda)$ which is a maximum when

$$\pi l/\lambda = 0 \text{ or } n\pi,$$

where n is an integer. Hence, since $a = 2\pi W/\lambda$ and $a' = 2\pi H/\lambda$, the condition for maximum current reduces to

$$a + a' = n\pi \quad \dots\dots(11)*.$$

If, as before, we take W/λ to be abscissae and H/λ to be ordinates, then equation (11) is represented by a series of straight lines cutting the axes at 45° . These are the curves (b) in figure 1. Hence we must conclude that if the frame-dimensions satisfy a point on any of the curves drawn in figure 1, then an abnormally large current will circulate round the frame.

Equation (11) may be written $l = n\lambda$.

Thus maximum frame current occurs when the frame-perimeter is an integral number of wave-lengths. This is also the condition for the formation of stationary waves such that the current nodes and antinodes are equally spaced round the frame, the number of nodes or antinodes being $2n$.

The experiments which were carried out to test the above theory will now be described.

§ 3. FRAME CURRENT MEASUREMENTS

Apparatus. Since the foregoing theory applies to frames comparable in dimensions with the wave-length, it is necessary to work with short waves, so that the size of the frame can be within reasonable limits. The oscillator had a wave-length range of 5.5 to 11.4 metres. The circuit is shown in figure 2, whilst figure 3 shows

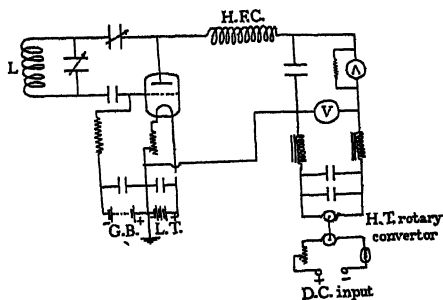


Figure 2.

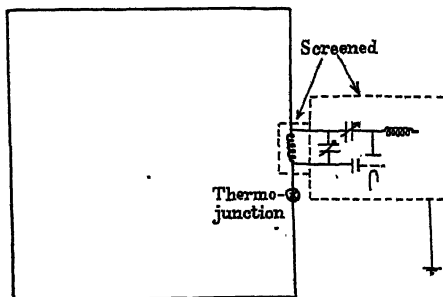


Figure 3.

the method by which the inductance L was directly coupled to the frame aerial. This inductance was a short strip of copper and formed a part of the frame. Because

* The same condition may be deduced by considering the effect produced by an infinite number of waves travelling round and round the frame. This method is employed in the following paper, pp. 76-84 of this issue.

of the small reactance-value of this strip compared with that of the frame, the tuning of the frame was not appreciably altered when the size of the frame was changed. The whole of the oscillator, including the inductance L , was screened by enclosing it in a sealed metal box. The current was measured with a thermo-junction and microammeter, which was read from a distance through a telescope.

The frame could be expanded or contracted in either or both dimensions by a modification of the method described by Palmer and Honeyball*. The new mechanism was so devised that all the necessary changes could be carried out from a distance of several wave-lengths. Errors arising from the movement of people in the vicinity of the aerial were thus obviated.

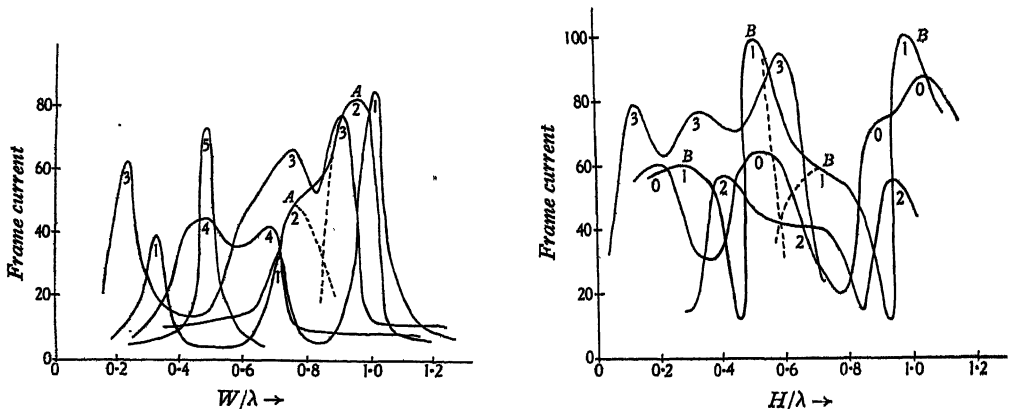


Figure 4. $\lambda = 5.85$ m. (1) $H/\lambda = 0.14$; (2) $H/\lambda = 0.35$; (3) $H/\lambda = 0.52$; (4) $H/\lambda = 0.72$; (5) $H/\lambda = 0.94$.
Figure 5. $\lambda = 5.9$ m. (0) $W/\lambda = 0.17$; (1) $W/\lambda = 0.3$; (2) $W/\lambda = 0.51$; (3) $W/\lambda = 0.83$.

Experimental measurements. In order to test the theory outlined in § 2 three methods were adopted. The general procedure in the first method was to take readings of the frame current for various widths, keeping the height of the frame and the radiated wave-length constant. Usually, readings were observed for every 20-cm. variation of the width. The measurements were repeated for frames of different heights varying from 1 to 6 metres. Figure 4 shows a set of results obtained in this way.

The procedure in the second method was exactly the same as in the first, but instead of the width, the height was varied. Some results obtained by this method are depicted in figure 5.

In the third method the frame current was recorded as before, but the size of the frame was kept fixed whilst the length of the radiated wave was varied by altering the tuning condenser of the oscillator. The wave-length was determined by an absorption wave-meter which had been calibrated from Lecher wires. Figure 6 shows the kind of results obtained, but these curves are less reliable than those shown in figures 4 and 5 because it was necessary for the operator to work near the aerial.

* *Proc. Inst. Radio Eng.* 20, 1357 (1932).

The curves in figures 4, 5 and 6 illustrate the very marked current changes obtained. Examination of figures 4 and 5 shows that the curves obtained in this way are often far from regular. The curve marked *A*, figure 4, obtained with a height equal to 0.35λ , and the curve marked *B*, figure 5, obtained with a width equal to 0.36λ , are good examples of this irregularity. The irregularity can be explained by resolving such peaks into two smooth curves, and it is then found that one peak corresponds to the position given by the first formatizing conditions and the other peak corresponds to the position given by the second formatizing conditions. Thus the positions of the resolved peaks appear to conform to the theoretical requirements for maximum current. Hence in order to test the theory given in § 2 it will be necessary to resolve all such irregular curves into their

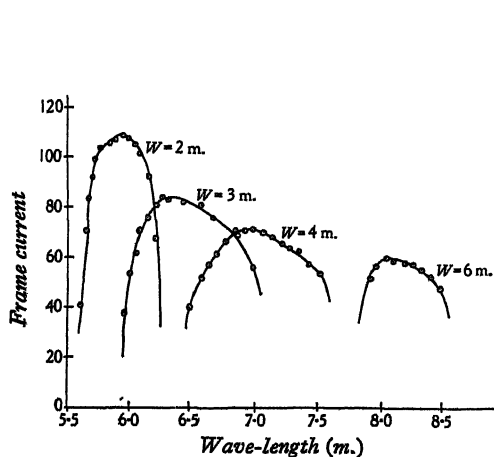


Figure 6. Height of frame, 5 m.

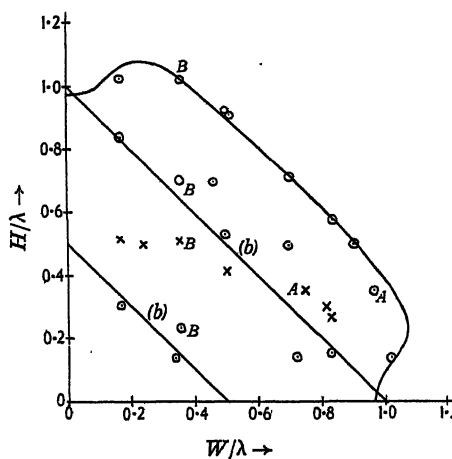


Figure 7.

components. The actual components in these two cases are shown dotted. This particular peculiarity is interesting in that it enables one to say which is the more potent factor in producing a large current—the first formatizing condition or the second formatizing condition. In every case it will be found that the first formatizing condition is by far the more important in these experiments.

It remains to be seen whether the actual positions of all the peaks approximate to those predicted by the theory. To test this point the peak values of H/λ and W/λ were calculated and plotted. The requisite data were obtained from figures 4, 5 and 6. Figure 7 shows the result of this analysis. For comparison, the theoretical curves of figure 1 have been added to the diagram. From the positions of the points marked with circles it appears that the theory given in § 2 is approximately correct. Experimental points have been found which lie on all the theoretical curves given in figure 1. In addition, however, certain experimental points, marked \times , do not lie on any of the theoretical curves. The explanation of these points appears to be as follows.

Reflection effects. In the theoretical discussion in § 2 the frame was considered

to be well removed from the influence of all other bodies. This does not obtain in the present instance, because the bottom of the frame was only about four feet above the ground. Since the ground, especially when wet, is a conductor, it will reflect electromagnetic waves incident upon it. Hence it is possible that the waves radiated from the frame may be reflected at the earth's surface and then received again by the frame. Under these circumstances the waves reflected back to the frame will be incident at an angle γ equal to 90° (with the nomenclature of the previous paper*), and consequently the frame will receive these reflected waves best (that is to say it will be formatized for these waves) when the frame-dimensions satisfy equations (1) and (2) in which $\gamma = 90^\circ$. With this condition these two equations reduce to

$$\tan(a - \psi) = (a^2 - 1)/a \quad \dots\dots(12)$$

and

$$\tan(2a' + \psi) = (a'^2 - 1)/a' \quad \dots\dots(13).$$

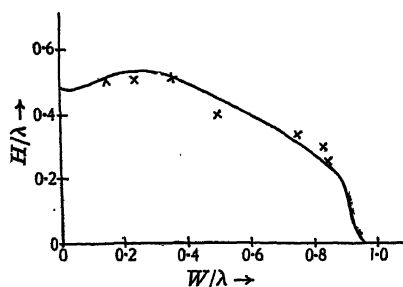


Figure 8.

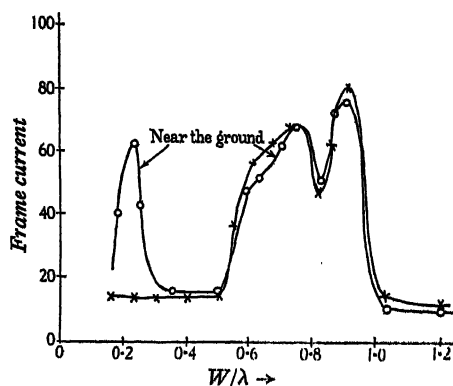


Figure 9. $\lambda = 5.85$ m. $H = 0.51 \lambda$.

The solutions of these equations for different values of ψ are plotted in figure 8. In the same figure are shown the unexplained experimental points of figure 7, and it seems apparent from the graph that these experimental points are due to the presence of waves reflected off the ground. In order to test the point fully, however, some additional experiments were carried out.

The procedure in these experiments was to record the variation of frame current with changing width as the frame of constant height was elevated to different distances from the ground. The experimental arrangements allowed the whole frame and oscillator to be raised to various heights up to 16 m. In this way, true current-maxima due to the formatizing conditions would remain unaltered, whilst effects due to reflection from the ground should become less and less marked as the frame is elevated.

The results of such an experiment for a frame of height 0.51λ are shown in figure 9. From these graphs it is apparent that the elevation was sufficient to cause one peak to disappear completely; the peak in question is marked by the second cross from the left in figures 7 and 8. In other experiments these subsidiary peaks

* *Loc. cit.*

could be intensified by artificially soaking the ground with water. The wetter the surface the stronger was the peak, whilst the other peaks remained unaffected. This is in agreement with the suggestion that these subsidiary peaks are caused by waves reflected from the ground.

Results. The results of the three experimental methods described in this section may now be summarized.

Experiments involving the variation of either the height or width of the frame or the wave-length lead to the same conclusion; namely, that maximum frame current is produced when either the first or second formatizing conditions are satisfied; i.e. when either equations (9) and (10) are satisfied or equation (11) is satisfied. In addition, the reflection experiments show that the frame current may also be a maximum when the conditions given by equations (12) and (13) are fulfilled.

§ 4. THEORETICAL CONDITIONS FOR MAXIMUM RADIATION

In the present paper consideration will be restricted to the case of transmission along the earth's surface in the direction of the plane of the frame. With this limitation the conditions necessary for maximum radiation from a transmitting frame are (1) large frame current, and (2) the correct co-phasing of the component fields at the particular point P (say) on the earth's surface at which the radiation is being received.

Conversely, the radiation to P will be small if either the frame current be small or the fields at P due to the currents in the several limbs of the frame be not in phase.

Equations (9) and (10) and equation (11) give the conditions for maximum frame current, whilst equations (1) and (2), with γ equal to 0 since P is on the earth's surface, give by the reciprocity theorem the conditions for the component fields at P to be in phase. The graphs of all these equations are shown in figure 10, which may be compared with figure 1. From figure 10 it is apparent that equations (9) and (10) and equations (1) and (2) are simultaneously satisfied only at the points of intersection A . Consequently, only for a transmitting frame of these particular dimensions (namely one in which $H/\lambda = 0.40$ and $W/\lambda = 1.00$ for the upper point and $H/\lambda = 0.09^*$ and $W/\lambda = 1.00$ for the lower point) will the radiation be good. For other frame-dimensions given by equations (9) and (10) the current will be large but the fields due to the current in parallel limbs will not completely reinforce at P , and hence the received radiation at P will be less.

Turning now to equation (11) which gives the condition for stationary waves; the graph of this equation has also solutions in common with those of equations (1) and (2), but in this case radiation is not to be expected as a result of the fulfilment of the stipulated conditions. The reason for this has been discussed by Macdonald†

* This dimension is less than 0.2 and consequently is outside the limits of accuracy of the present theory.

† Macdonald, *Electric Waves*, p. 62 *et seq.* (Cambridge University Press).

who shows that, when the frame-perimeter is an integral number of wave-lengths, then the fundamental free period of the frame is the same as the period of the applied e.m.f. The resulting oscillations are said to be *permanent* and there is no radiation from the frame. This will be the case whether the conditions given by equations (1) and (2) are fulfilled or not, and hence no radiation will be apparent when such permanent oscillations are present in the frame.

Owing to the reflection effects discussed in § 3, the transmitting frame will also have a large current in it when its dimensions satisfy equations (1) and (2) in which $\gamma = 90^\circ$, i.e. when equations (12) and (13) are satisfied. If the graphs of these equations be plotted along with that for maximum radiation along the ground—i.e.

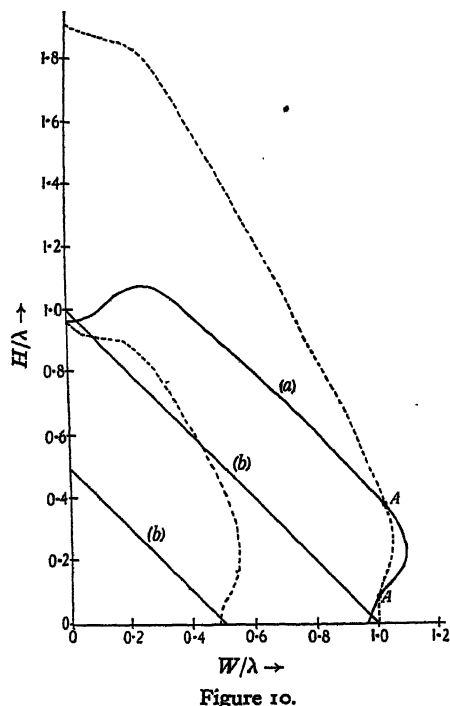


Figure 10.

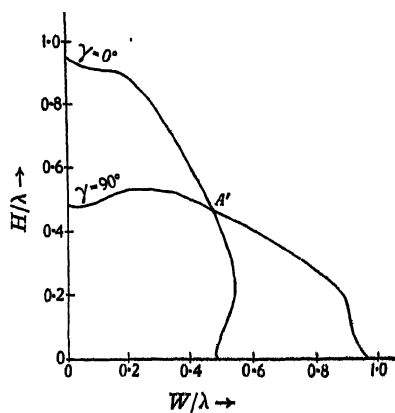


Figure 11.

equations (1) and (2) when $\gamma = 0^\circ$ —then it will be seen that at the point A' in figure 11 the two conditions are satisfied simultaneously. Thus, for the square frame of these particular dimensions (namely, $H = W = 0.47\lambda$) a large radiation field may be expected at points along the earth's surface if reflected waves are appreciably affecting the frame current.

§ 5. HERTZIAN-RECEIVING-ROD MEASUREMENTS

The conditions for maximum radiation were tested by measuring the radiation from the frame with a Hertzian-rod receiver. The receiver used was similar to that already described by one of us*, and was situated in the same vertical plane as

* Palmer and Honeyball, *J. Inst. E.E.* 67, 1049 (1929).

the frame at a distance of several wave-lengths. The microammeter deflections were read by means of a telescope by an observer lying on the ground at the foot of the receiver.

For constant frame-widths, the transmitting-frame current and the current received by the tuned Hertzian rod were recorded for different values of the frame-height, the wave-length remaining constant. Each set of readings were repeated for frame-widths of from 1 to 6 metres. The frame-current variations have already been discussed in the previous sections, and figure 12 shows a typical set of Hertzian-rod current-values plotted against the varying height of the transmitting frame. The critical frame-dimensions, in terms of H/λ and W/λ , for which the Hertzian-rod currents were a maximum, are plotted in figure 13 together with the theoretical curves from figures 10 and 11. The points in figure 13 are numbered to correspond with the peaks in figure 12 to which they refer.

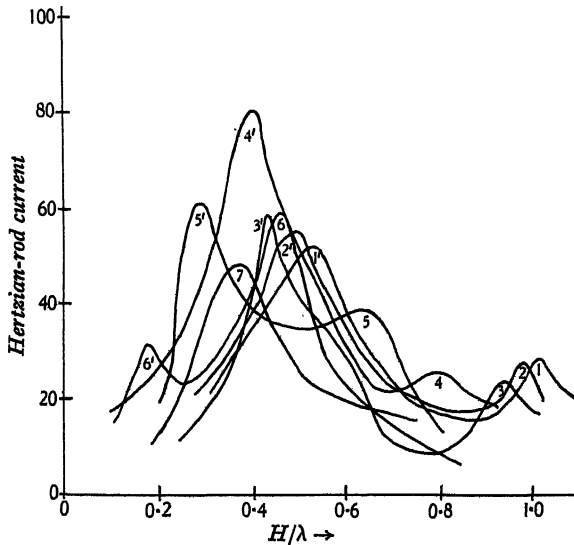


Figure 12. Radiation-measurements.

$\lambda = 5.9$ m. (1) $W/\lambda = 0.17$; (2) $W/\lambda = 0.36$; (3) $W/\lambda = 0.497$; (4) $W/\lambda = 0.52$;
(5) $W/\lambda = 0.66$; (6) $W/\lambda = 0.88$; (7) $W/\lambda = 1.04$.

The conclusions arising from a consideration of these two figures may now be summarized as follows. (1) There are in general, for each value of the frame-width, two critical values of the height less than one wave-length for which the radiation is a maximum. The taller frame has the critical dimensions predicted by the first formatizing conditions, whilst the dimensions of the shorter frame are such that it is formatized for the reception of waves reflected from the ground. (2) There are no experimental points on the curves (b). That is to say, there is no radiation from frames the dimensions of which fulfil the second formatizing condition, or the perimeters of which are integral numbers of wave-lengths. If the Hertzian-rod currents are plotted on the same graph as the transmitting-frame currents, as in

figure 14, the absence of radiation when such stationary waves occur in the frame is more readily seen than from such curves as those of figure 12 where the Hertzian-rod currents alone are depicted. (3) Peaks 6 and 4' in figure 12 show that the greatest radiation occurs from the frames the dimensions of which are given by the co-ordinates of these particular points in figure 13. The greatest radiation was anticipated on pages 71 and 72 from frames the dimensions of which are given by points A and A' ; and it is significant that points 6 and 4' lie close to these respective theoretical positions. Actually points 7 and 3' lie somewhat closer to A and A'^* , but it is thought that this discrepancy is an experimental error arising from the

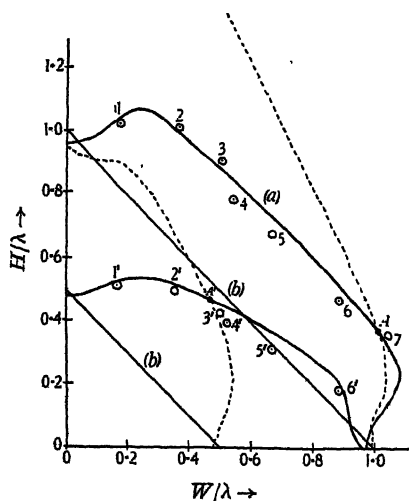
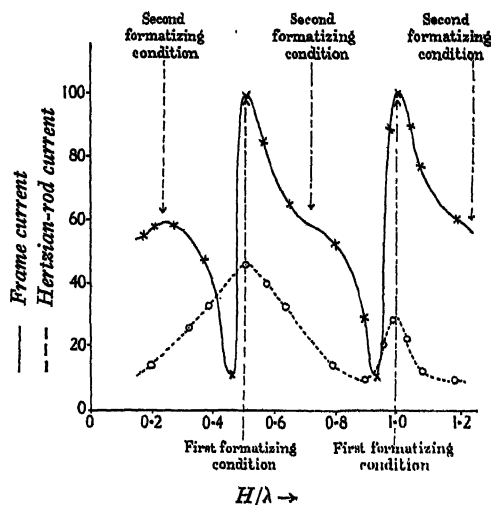


Figure 13.

Figure 14. $\lambda = 5.5$ m. $W/\lambda = 0.36$.

difficulties inherent in these short-wave measurements. It is felt that perhaps the most crucial test of the foregoing theory is the marked increase in the radiation from frames the dimensions of which approximate to the theoretical values indicated by the co-ordinates of the points A and A' ; whilst the fact that all the experimental

* Walmsley and Bewick in *G.P.O. Radio Report*, No. 211, of November 1931, record some tests which they carried out in order to verify certain preliminary conclusions published by Palmer and Honeyball in a letter to *Nature*, March 14, 1931. Walmsley and Bewick obtained maximum radiation from a square frame for which $H = W = 0.50\lambda$ in one set of measurements and for which $H = W = 0.47\lambda$ in a second set of measurements. They conclude: "From an examination of all the results it is evident that the size of frame is not very critical and that for all practical purposes there is no advantage in departing from the normal $.5\lambda$ square size of frame." They thus assume that their results are in accord with the old theory which stated that the frame current should be a maximum when the frame dimensions were equal to half a wave-length. Not only is this theory incorrect, but no radiation will occur if these conditions are exactly fulfilled. As their frame was only 4 ft. from the ground, their result is probably due to unsuspected reflected waves, and seems to be a further confirmation of the abnormal radiation predicted by the above theory for the square frame of sides equal to 0.47λ —a result which they actually obtained in one set of measurements. Walmsley and Bewick's largest frame was only 0.56λ wide and hence they missed the large radiation which occurs when the frame-dimensions are given by the co-ordinates of the point A in figure 13.

points lie on the graphs of the equations of the first formatizing condition, but not on the graphs of the equation of the second formatizing condition, seems to give further support to the theory outlined in §§ 2, 4.

§ 6. CONCLUSIONS

(1) From the experiments described in § 3 it is concluded that variations in the dimensions of a tuned transmitting frame will appreciably affect the frame current and that the current will be a maximum only for certain critical values of the ratios of the dimensions of the frame to the length of the wave.

The critical frame-dimensions for the production of maximum current by a local oscillator are given approximately by the equations

$$\tan(a - \psi) = (a^2 - 1)/a \quad \text{..... (9)}$$

and

$$\tan(a' + \psi) = (a'^2 - 1)/a' \quad \text{.....(10)}$$

and also by equations (12) and (13) if waves reflected normally from the ground affect the frame current.

Less important frame-current maxima occur when

$$a + a' = n\pi \quad \text{.....(11).}$$

This is the condition for the establishment of "permanent" oscillations or stationary waves round the frame with equally spaced nodes and antinodes.

(2) The experiments with the Hertzian-rod receiver, § 5, indicate that large radiation is obtained at points on the earth's surface in the plane of the frame when equations (9) and (10), or equations (12) and (13), are satisfied; but that the best radiation occurs when these equations, and also equations (1) and (2) with γ equal to 0, are simultaneously satisfied. That is to say, the best dimensions of a frame for horizontal radiation are:

$$H = 0.40\lambda \text{ and } W = 1.00\lambda \text{ (point } A, \text{ figure 13).}$$

With the effect of the reflected waves from the ground, additional dimensions for good radiation are:

$$H = W = 0.47\lambda \text{ (point } A', \text{ figure 13).}$$

(3) No radiation perpendicular to the sides of the frame occurs when the frame-perimeter is an integral number of wave-lengths, i.e. when

$$a + a' = n\pi \quad \text{.....(11).}$$

§ 7. ACKNOWLEDGMENTS

We should like to record our thanks to Mr R. Curry for assistance in carrying out this work, and also to Mr R. A. Watson-Watt who kindly loaned the short-wave oscillator used in the experiments.

DISCUSSION

See page 87.

THE CURRENT-DISTRIBUTION ROUND A SHORT-WAVE FRAME AERIAL

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ABSTRACT. On the assumption that an initial oscillation in any part of a frame aerial is propagated round and round the frame an infinite number of times in both directions, with the consequent formation of stationary waves, a theoretical expression is obtained for the value of the current in any part of the frame. From the expression so obtained the positions and magnitudes of the current antinodes are deduced. The antinodes are fixed in space and are independent of the orientation of the frame to the wave-front. The current at any point of a frame consequently varies as the frame revolves in its own plane.

Experimental results are described which verify the conclusions concerning the positions of the antinodes and the effects produced by a revolving frame. Other experiments are in progress to test the deductions concerning the magnitudes of the currents at the antinodes.

§ 1. INTRODUCTION

IN the previous paper* it was shown that the current produced in a tuned rectangular frame by a passing electromagnetic wave or by a local oscillator attained its maximum values when the ratio of the frame-dimensions to the wave-length was critically adjusted in accordance with the solutions of either of two equations.

In the case of a receiving frame actuated by an electromagnetic wave, the critical dimensions are given by

$$\text{either} \quad \left\{ \begin{array}{l} \tan [a (1 + \cos \gamma) - \psi] = (a^2 - 1)/a \\ \tan [a' (1 + \sin \gamma) + \psi] = (a'^2 - 1)/a' \end{array} \right\} \quad \dots\dots(1),$$

$$\text{or} \quad a + a' = n\pi \quad \dots\dots(2),$$

where $a = 2\pi W/\lambda$, $a' = 2\pi H/\lambda$, n is an integer, W is the frame-width, H is the frame-height, λ is the wave-length, γ is the angle of incidence of the wave-front to the frame and ψ is an arbitrary phase angle.

The corresponding equations for a transmitting frame actuated by a local oscillator are

$$\text{either} \quad \left\{ \begin{array}{l} \tan (a + \psi) = (a^2 - 1)/a \\ \tan (a' - \psi) = (a'^2 - 1)/a' \end{array} \right\} \quad \dots\dots(3),$$

$$\text{or} \quad a + a' = n\pi \quad \dots\dots(2).$$

* Page 62 of this volume.

These sets of equations give what were called for convenience the first and second formatizing conditions for reception and transmission respectively.

When testing these equations experimentally it was found that the maximum currents which resulted when the frame was formatized were not uniformly distributed round the frame and that the current registered at any one point was not necessarily the same as that recorded elsewhere in the frame. Notwithstanding this spacial variation, the current at any given point did, in general, attain its maximum value when the frame-dimensions approximated to the solutions of either of the above equations.

In order to understand more fully the action of a short-wave frame aerial, it was thought desirable to investigate the current-distribution round a frame as the ratio of its dimensions to the wave-length varied.

It has already been stated in the previous paper that the second formatizing condition may be written

$$l = n\lambda,$$

where l is the frame-perimeter. From this it follows that stationary waves will be so formed that there will be $2n$ nodes and antinodes equally distributed round the frame, but there is no indication from this equation how these nodes and antinodes will be located with respect to the corners of the frame, or the position of the tuning condenser, or the position of the initial e.m.f. Neither is there any indication which of these three factors, if any, fixes the positions of the nodes and antinodes.

The first formatizing condition makes no stipulation as to the ratio of the frame-perimeter to the wave-length, and in general $l \neq n\lambda$ for the maximum currents given by equations (1) and (3). The problem thus resolves itself into a determination of the current-distribution round a short-wave frame aerial for the general case when the ratio of the frame-perimeter to the wave-length is not an integer. The current-distribution for the second formatizing condition given by equation (2), for which this ratio is an integer, will then be a special case of the more general solution.

§ 2. THEORETICAL CONSIDERATIONS

The action of a short-wave frame aerial. When an incident wave or a local oscillator actuates a frame aerial at a given point P , figure 1, the electric force causes a charge at P to oscillate to and fro at the wave frequency. The resulting disturbance travels round the frame with approximately the velocity of the wave in the surrounding medium. For convenience, the wave may be looked upon as starting off in one direction as a compression wave at the same time that it starts off in the opposite direction as a rarefaction wave. These two impulses will meet half-way round the frame at P' where they will both tend to accelerate a charge in the same direction; that is, their effects will reinforce each other, but will not necessarily be in phase with the disturbance at P' due directly to the passing wave, and a continuous disturbance will result at P' as long as the initial oscillation is maintained at P . These waves will continue round the frame and meet again at P where they

will again be in phase with each other, but not necessarily with the existing oscillation at P . In general, before they reach P , they will be met at Q_1 and Q_1' , say, by the second impulses which started from P one period later and are now travelling away from P . At Q_1 the first compression impulse, say, from P will meet and reinforce the second rarefaction impulse from P , and vice versa at Q_1' . The time for the disturbances to travel from P to Q_1 by way of Q_1' and P' will be one period of the oscillation plus the time taken for the second impulse to travel from P to Q_1 directly. These two impulses at Q_1 (or Q_1') will be in phase and reinforce each other. Thus the disturbance at Q_1 (or Q_1') will reinforce when $l - x_1 = \lambda + x_1$, where l is the frame-perimeter and x_1 is the distance PQ_1 measured the shortest way round the frame.

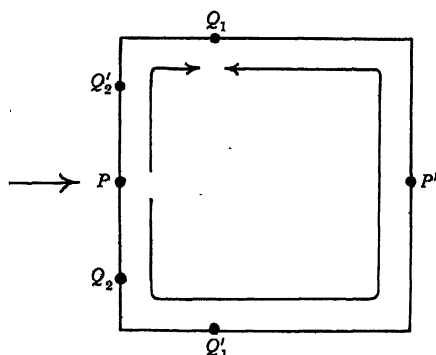


Figure 1.

In general, the two disturbances will have different amplitudes owing to the fact that the first disturbance will have travelled $(l - 2x_1)$ or λ round the frame farther than the second disturbance. These waves will continue to travel round and round in opposite directions and return to Q_1 (or Q_1') again in phase with each other, but with a further reduction in amplitude due to the loss during a complete circuit of the frame. Similarly, any two consecutive impulses at P will always reinforce each other at Q_1 and Q_1' .

By a similar argument it follows that alternate impulses at P will reinforce at points Q_2 and Q_2' at a distance x_2 from P given by

$$l - x_2 = 2\lambda + x_2.$$

But with these current antinodes the amplitude of the disturbance will be smaller owing to the greater damping which will have resulted from the fact that the first impulse will have travelled a distance $(l - 2x_2)$ or 2λ farther than the third impulse.

In general, current antinodes with amplitudes decreasing with n will occur at distances x_n from P (or at distances $n\lambda/2$ from P') given by

$$x_n = \frac{1}{2}(l \pm n\lambda).$$

This equation may be written

$$a + a' - \delta_n = \pm n\pi \quad \dots\dots(4),$$

where $\delta_n = 2\pi x_n/\lambda$ and the other symbols have the meanings indicated on p. 76.

A more complete treatment of the problem is as follows. Let the initial disturbance at P be $I_0 \sin \omega t$ and let the damping due to the path length of λ be η and that due to one circuit of the frame be ϵ , where η and ϵ are both less than unity. Then the resultant current at points Q_n and Q_n' due to the first reinforcement of the two impulses will be

$$I_0 \sin \{\omega t - (\delta_n + 2n\pi)\} + \eta^n I_0 \sin \{\omega t - (\beta - \delta_n)\}, \\ = I_0 \sqrt{\{1 + 2\eta^n \cos (\beta - 2\delta_n) + \eta^{2n}\} \cdot \sin (\omega t - \delta_n - \theta)},$$

where $\beta = 2\pi l/\lambda$ and $\theta = \tan^{-1} \frac{\eta^n \sin (\beta - 2\delta_n)}{1 + \eta^n \cos (\beta - 2\delta_n)}$.

These two waves will each complete a circuit of the frame and arrive back at Q_n (or Q_n') again with an additional phase-lag β and with a reduced amplitude ϵI_0 .

Hence the resultant effect of these two waves will be

$$\epsilon I_0 \sqrt{\{1 + 2\eta^n \cos (\beta - 2\delta_n) + \eta^{2n}\} \cdot \sin (\omega t - \delta_n - \theta - \beta)}.$$

For the next circuit the resultant at Q_n (and Q_n') will be

$$\epsilon^2 I_0 \sqrt{\{1 + 2\eta^n \cos (\beta - 2\delta_n) + \eta^{2n}\} \cdot \sin (\omega t - \delta_n - \theta - 2\beta)},$$

and the final result I at Q_n (and Q_n') is therefore

$$\sum_{Z=0}^{Z=\infty} \epsilon^Z I_0 \sqrt{\{1 + 2\eta^n \cos (\beta - 2\delta_n) + \eta^{2n}\} \cdot \sin (\omega t - \delta_n - \theta - Z\beta)} \\ = I_0 \sqrt{\left\{ \frac{1 + 2\eta^n \cos (\beta - 2\delta_n) + \eta^{2n}}{1 - 2\epsilon \cos \beta + \epsilon^2} \right\} \sin (\omega t - \delta_n - \theta - \theta')} \quad \dots\dots(5),$$

where $\theta' = \tan^{-1} \frac{\epsilon \cdot \sin \beta}{1 - \epsilon \cos \beta}$.

Since the signs of the cosine terms in the numerator and denominator are plus and minus respectively, the amplitude of the current I is a maximum when either

$$\beta = 0 \text{ or } \pm 2n\pi,$$

i.e. $a + a' = \pm n\pi \quad \dots\dots(2),$

or $\beta - 2\delta_n = 0 \text{ or } \pm 2n\pi,$

i.e. $a + a' - \delta_n = \pm n\pi \quad \dots\dots(4).$

Thus we recover equations (2) and (4) as before. It also follows from equation (5) that the values of the current maxima are not the same for the two conditions. When the former condition holds, then the amplitude of the current antinode is given by

$$I_{1(\max)} = \frac{I_0 \sqrt{\{1 + 2\eta^n \cos 2\delta_n + \eta^{2n}\}}}{1 - \epsilon} \quad \dots\dots(6),$$

which becomes infinite when $\epsilon = \eta = 1$ or damping is neglected.

When the second condition, equation (4), is fulfilled, then the maximum amplitude is

$$I_{2(\max)} = \frac{I_0 (1 + \eta^n)}{\sqrt{\{1 - 2\epsilon \cos 2\delta_n + \epsilon^2\}}} \quad \dots\dots(7),$$

which becomes $I_0 \operatorname{cosec} \delta_n$ when $\epsilon = \eta = 1$.

Some of the conclusions which follow from the interpretation of these equations will now be considered.

Some consequences. Deductions from the foregoing equations may conveniently be divided into those which concern the location of current antinodes round a frame and those which concern the magnitude of the current at the antinodes.

Since equation (2) is equation (4) with x_n equal to $\pm \frac{1}{2}n\lambda$, it follows that all the antinodes are spaced $\frac{1}{2}\lambda$ apart when the ratio of the frame-perimeter to the wavelength is an integer. Further, the first antinode, when $x = 0$, is at P , the point where the initial disturbance was produced. This will normally be the point of the frame nearest to the transmitter, or the point to which a local oscillator is coupled. Equation (2) has already been discussed at some length in previous papers. It has been called the "second formatizing condition." The justification for this may be seen from equation (6) which shows that, when the conditions given by equation (2) are fulfilled, the maximum amplitude of the current antinodes tends to be infinite, and is only limited by resistance damping. Thus the frame functions as a non-reactive and non-radiating circuit with ohmic resistance only.

Equation (4) has not been discussed hitherto and will therefore be considered in greater detail. There are, in particular, six conclusions concerning the frame current which call for consideration and experimental verification. The first four concern the location of the current antinodes and the last two deal with the current amplitudes. These six points are: (i) All the current antinodes are at fixed distances from P , which is a fixed point determined by the position of the initial disturbance. Hence the distribution of nodes and antinodes round a frame aerial is fixed in space and is independent of the orientation of the frame to the wave-front. (ii) The disposition of the current nodes and antinodes is symmetrical about the line PP' , figure 1. (iii) Current antinodes always occur at P and P' irrespective of the wavelength. This follows because $x = \frac{1}{2}P$ when $n = 0$. (iv) Successive current antinodes are $\frac{1}{2}n\lambda$ from P' measured in both directions round the frame. (v) The amplitudes of the current at successive antinodes decrease to a minimum (I_0 if damping be neglected) as the distance x_n of the antinode from P increases, until this distance equals $\frac{1}{4}\lambda$, after which the current peak values gradually increase to a maximum (∞ if damping be neglected) when the value of x_n reaches $\frac{1}{2}\lambda$. This conclusion follows from equation (7), which shows that the amplitude is equal to $I_0 \operatorname{cosec} [f(x_n)]$ when $\epsilon = \eta = 1$. (vi) For large values of n , the value of $I_{2(\max)}$, equation (7), decreases so that only the first few current antinodes may be readily detected in practice.

Finally, there is another consequence which follows indirectly from point (i) above. Since the nodes and antinodes are fixed in space, the current at any particular point in a frame aerial will vary as the frame revolves in its own plane, but the current will be constant for any point in the revolving frame when the point in question passes through any particular point in space. In other words, if a current-measuring instrument be fixed in a revolving frame aerial it will, apart from any other factors not here considered, record the current-values of the various nodes and antinodes as it passes through the points $P, Q_2, Q_1', P', Q_1, Q_2'$, in succession. Also, if the instrument be fixed in space, the recorded current will be constant as

the frame revolves, the current value depending on the position of the instrument with respect to the transmitter or to the fixed points P and P' .

The experimental verification of the above six points and of the conclusions concerning a revolving frame would be a comparatively easy matter were it not for the fact that other disturbing factors may arise which tend to modify the experimental measurements. The chief of these factors is the current-variation caused by the fulfilment of the first formatizing conditions.

By employing a frame which is always deformatized from this standpoint—that is to say, by using a frame the dimensions of which do not satisfy equations (1) or (3)—it is possible to study the current-distribution which has been discussed above and to isolate one set of effects from the other.

§ 3. EXPERIMENTAL INVESTIGATION

Preliminary experiments have been carried out with a square frame of perimeter 12·24 m., and so arranged that the wire could slide over insulated pulleys fixed on the corners of the supporting wooden framework. Thus a vacuum thermojunction inserted at any point could either move round with the frame or remain fixed in space as the wooden framework moved, leaving the wire stationary.

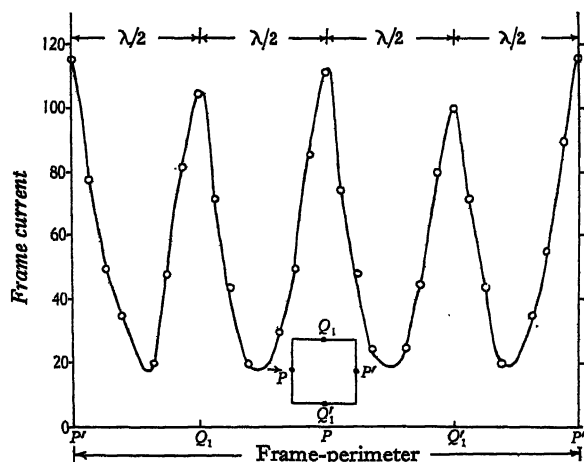


Figure 2. Fixed frame. $\lambda = 6\cdot12$ metres.

Some results are shown in figures 2 to 10. Figures 2 and 3 were obtained by moving a current-measuring instrument round a receiving frame which was fixed with one side nearest to the transmitter. Figure 2 is an illustration of the current-distribution when the frame-perimeter is an integral number of wave-lengths in accordance with equation (2), whilst figure 3 depicts the current-distribution when the ratio of the frame-perimeter to the wave-length is not an integer. Equation (4) is applicable to this case. These two figures show the fixed current antinodes at P and P' and the movement of the other antinodes Q_1 and Q_1' away from P' as the

wave-length increases. In each case the distances $P'Q_1$ and $P'Q_1'$ equal approximately $\frac{1}{2}\lambda$.

In figures 4 and 5 the circles show the theoretical positions, from equations (2) and (4), of the current antinodes, and the crosses show the experimental positions as determined from figures 2 and 3.

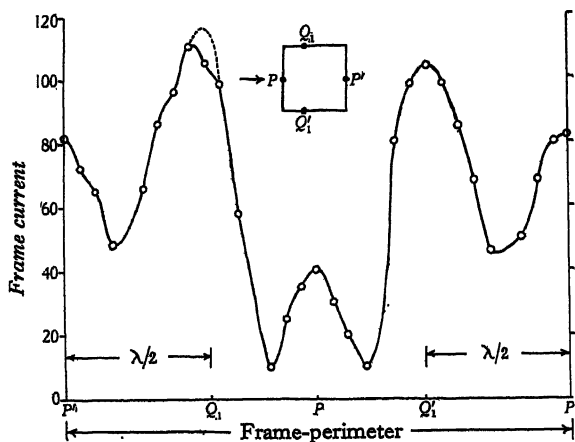


Figure 3. Fixed frame. $\lambda = 7.3$ metres.

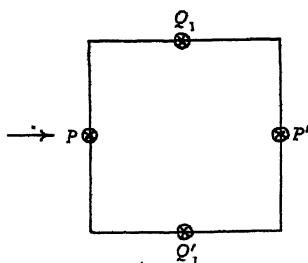


Figure 4. \odot Theory. \times Experiment.
 $\lambda = 6.12$ metres.

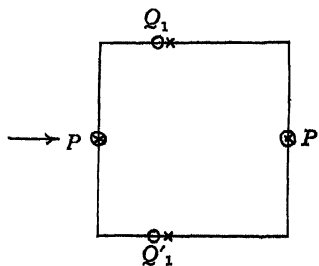


Figure 5. \odot Theory. \times Experiment.
 $\lambda = 7.3$ metres.

Figure 6 is a repetition of figure 3 with the frame oriented with one corner nearest to the transmitter. The comparison of this figure and figure 7 with figures 3 and 5 respectively shows the fixity of the current-distribution in space, irrespective of the orientation of the frame.

Figures 8, 9 and 10 were obtained with a revolving frame. Figure 8 is a reproduction of figure 2, but was obtained by rotating the frame together with the thermojunction. This again shows the fixity of the nodes and antinodes in space, but does not illustrate the current-variations predicted in a previous paper*, because the current-variations shown in figure 8 are not due to the frame becoming deformatized as it revolves. The frame remains formatized in accordance with the

* *Proc. R.S. A* 136, 193-209 (1932).

second formatizing condition, equation (2), and is always deformatized from the point of view of the requirements of equation (1). These current-variations are only due to the fixity of the positions of the current nodes and antinodes in space.

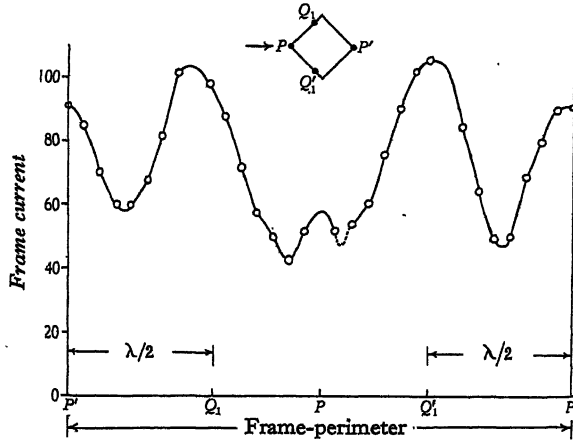


Figure 6. Fixed frame. $\lambda = 7.3$ metres.

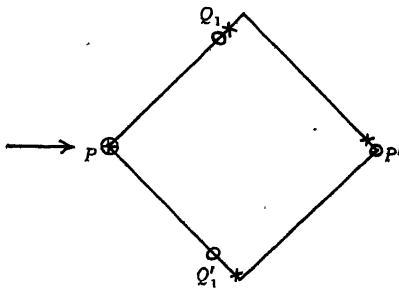


Figure 7. \odot Theory. \times Experiment.
 $\lambda = 7.3$ metres.

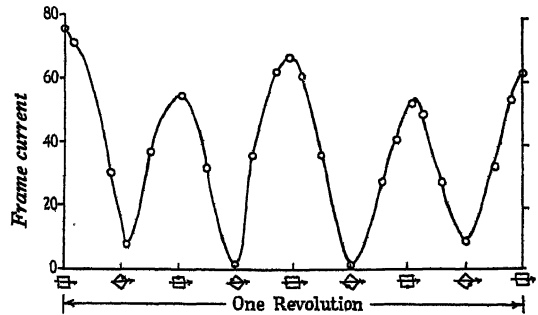


Figure 8. Revolving frame. $\lambda = 6.12$ metres.

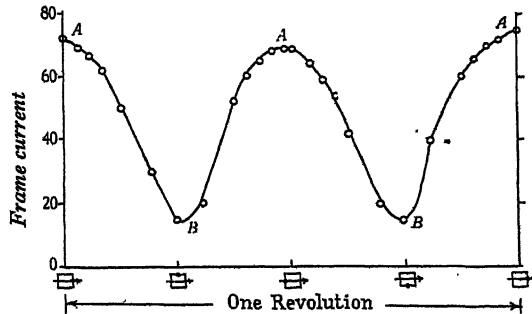


Figure 9. Revolving frame. $\lambda = 12.2$ metres.

Figure 9 is similar to figure 8, but the ratio of the perimeter to the wave-length is unity. The only antinodes are those at P and P' .

Finally, figure 10 confirms the conclusion that if a frame be rotated and the current-measuring instrument be fixed in space, then the measured current will remain constant and record a value depending on the distance of the instrument from the fixed points P and P' . The values of A and B in figure 10 refer respectively to the points A and B in figure 9, which indicate where the instrument was fixed.

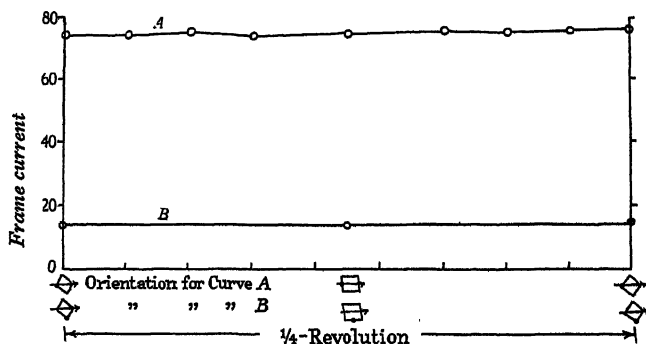


Figure 10. Revolving frame with instrument fixed in space. $\lambda = 12.2$ metres.

§ 4. CONCLUSIONS

The above preliminary experiments confirm the first four of the six points discussed in § 2 above, but there are not yet sufficient data to verify points (v) and (vi) concerning the magnitudes of the amplitude-variations. Further experiments to this end are now in progress. The experiments with the revolving frame are also in accordance with the conclusions deduced at the end of § 2 on pp. 80 and 81.

Hence it is concluded that, as long as the ratios of the frame-dimensions to the wave-length do not satisfy equations (1) or (3), equation (5) gives the position, and possibly the magnitudes, of the current antinodes round a short-wave frame aerial.

§ 5. ACKNOWLEDGMENT

We are pleased to record our thanks to Mr R. Curry, B.Sc., D.I.C., for assistance in carrying out the experiments.

DISCUSSION

See page 87.

DEMONSTRATION

Some experiments with ultra-short wireless waves in water. *Demonstration given on October 20, 1933 by Prof. L. S. PALMER, D. TAYLOR and ROY WITTY to illustrate papers on pages 62 and 76 entitled respectively "The action of a tuned rectangular frame aerial when transmitting short waves" and "The current-distribution round a short-wave frame aerial."*

In order to demonstrate the effects discussed in the two papers referred to above it is necessary to employ frame aerials comparable in dimensions with the length of the wireless wave in use. This necessity introduces two difficulties if the demonstrations are to be carried out in a lecture room. Firstly, the frames must be of such dimensions that they can be manipulated easily on a demonstration bench, and secondly, the radiated power from the short-wave transmitter must be sufficient to operate flash-lamp bulbs or other visible current indicators which may be inserted at various points round the frames where it is desirable to show the presence or otherwise of current antinodes. If the size of the frames be of the order of 10 or 20 cm., then the available power from any simple transmitter such as a Barkhausen valve oscillator operating on such short wave-lengths is insufficient. With wave-lengths greater than 3 m. the radiation can be adequate, but in this case the frames must be inconveniently large and therefore difficult to manipulate in a limited space.

It was found that both these difficulties could be overcome by using an ordinary valve oscillator operating on 3 m. or 4 m. (say) in air but coupled to a radiating half-wave Hertzian dipole immersed in a tank of water. Thus the radiated wave-length is reduced in the ratio of 1 to $1/\sqrt{K}$, where K is the dielectric constant of water for these frequencies. K is about 80, so that the normal wave-length range of 3 to 4 m. in air is only 33.6 to 44.7 cm. in water. With this method the available power is found to be ample for actuating small receiving frames of the order of 10 to 20 cm. in linear dimensions when immersed in the glass tank of water containing the radiating dipole. It is convenient to transmit vertically downwards by having the dipole arranged horizontally about a quarter of a wave-length below the surface of the water.

Figure 1 is a diagrammatic sketch of the actual apparatus in which the four essential parts of the transmitter are the power unit *A*, the valve oscillator *B*, the half-wave transmission line *C*, and the radiating dipole *D*. In addition there is the tank of water *E* containing the dipole *D* and the receiving frame *F*. The motor *G* revolves the frame in its own plane by suitable gearing.

The circuit diagram is shown in figure 2 in which the reference letters correspond with those in figure 1.

To show the current-distribution round different frame aerials when actuated by waves of different lengths, it is convenient to use circular frames with perimeters ranging from 1 to 2 wave-lengths, that is from about 40 to 80 cm. With a frame, the perimeter of which is equal to one wave-length, current antinodes occur at those

points of the frame which are nearest to and most remote from the dipole D . These are the antinodes marked P and P' on page 78 of the paper on "The current-distribution round a short-wave frame aerial." To indicate the positions of these antinodes (which are fixed in position) a flash-lamp bulb is inserted in the frame. The frame is mounted on a wooden support which can be revolved by the motor G fixed outside the tank. In this way, as the frame revolves in its own plane, so the flash-lamp bulb passes in succession through the fixed points P and P' , and in so doing it is momentarily lighted up. By the use of a frame with a perimeter greater than one wave-length, the positions of the additional antinodes Q and Q' can be observed. Also, if the wave-length be gradually increased, the resulting gradual motion of these antinodes away from P' can be detected by the variation in the positions at which the lamp becomes lighted.

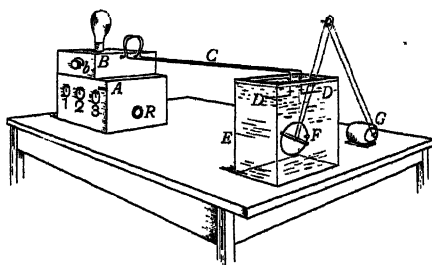


Figure 1

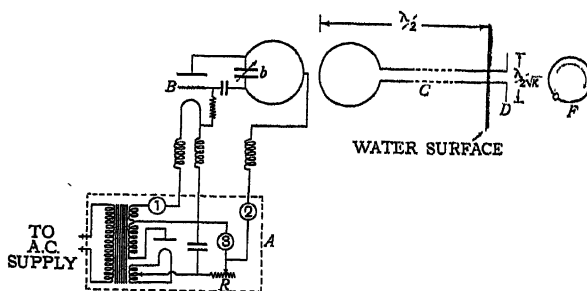


Figure 2

With a square or rectangular frame the same results are obtained whatever the positions of the lamp in the frame as long as the frame-dimensions compared with the wave-length are such that the frame remains deformatized* as it revolves. This can best be shown by taking a square frame with two flash-lamp bulbs in it, one in the middle of one side of the frame and one at a corner. Then, as each bulb passes in turn through the positions of the antinodes P or P' it lights up, and the intensity of the light from each bulb is the same.

To show the effect produced when a transmitting frame is formatized in accordance with the conditions given by equations (9) and (10)† is not practicable with this apparatus; but the effect of formatizing a receiving frame in accordance with

* *Loc. cit.* p. 62.† *Loc. cit.* p. 66.

equations (1) and (2) may be demonstrated by using a square frame with two flash-lamp bulbs inserted where indicated above. The frame-dimensions compared with the wave-length must be such that the frame is formatized when one side is parallel to the dipole D , i.e. when the frame is in the square position for which γ in the above equations (1) and (2) is equal to zero. Then, as the frame revolves the lamp in the side of the frame lights up more brightly than the lamp in the corner. This effect is reversed if the frame be of such dimensions that it is formatized in the diamond position with its sides at 45° to the dipole, i.e. if $\gamma = 45^\circ$ in equations (1) and (2). Thus although the antinodes remain fixed in space they do not remain constant in amplitude if the frame becomes alternately formatized and deformatized as it revolves.

For a wave-length of 3.8 m. in air or 42.5 cm. in water the sides of a square frame must be 20 cm. long for the frame to be formatized in the square position, whilst the sides of the frame must be only 16.5 cm. long for the frame to be formatized in the diamond position with this particular wave-length. These values may be deduced from figure 3 of a previous paper*.

These three experiments with square frames serve as a useful qualitative test of the theory which has been advanced to explain the anomalous effects obtained when rectangular frames are used with short waves.

By the use of the apparatus described above together with a small Hertzian dipole receiver with a flash-lamp bulb at its centre, the polarization of wireless waves and the changes produced on reflection from various surfaces may be readily demonstrated. With a sufficiently large tank, interference phenomena can be observed; and from the positions of the nodes and antinodes on Lecher wires in various liquids the dielectric constants and their variation with frequency may be measured. Because it is possible with this arrangement to illuminate flash-lamp bulbs, the apparatus is particularly convenient for demonstrating most of the properties of electromagnetic waves to large audiences.

DISCUSSION OF THE PRECEDING TWO PAPERS AND DEMONSTRATION

Dr R. L. SMITH-ROSE. The subject of frame aerials for the transmission and reception of short electric waves is one that is of considerable importance and interest to those concerned with radio communication. For ordinary frame-dimensions and medium wave-lengths the justifiable assumption is usually made that the ratio of height or width to wave-length is small. When, however, the wave-length is reduced to such an extent that this ratio is no longer small compared with unity, then certain effects outlined by Prof. Palmer in his previous papers become important and must be taken into account. Some of us have thought that the discussion of the subject given in these earlier papers was somewhat unsatisfactory, and we are therefore glad to see that the matter is being pursued further.

* L. S. Palmer, *Proc. R.S. A* 136, 199 (1932).

One of the points that has been cleared up is the question of the current-distribution around the frame, and (as the experiments clearly demonstrate) it is not sufficient to refer to the current in a frame without specifying the point at which the current is being measured, in addition to the wave-length and frame-dimensions. It would be interesting to know why the point P was selected at the centre of a vertical side in the theoretical analysis of the reception by a frame of an induced e.m.f. Presumably the incident electric force must be parallel to the side containing P . Is the location of P decided merely from conditions of symmetry? Since the frames do not include any tuning-condensers the current-distribution might be deduced from that in a transmission line or a Lecher wire system.

It would appear that the current-distribution in some of the cases illustrated in the paper could have been deduced from the suggestions of current-distribution in open wire aerials put forward by Korshenewsky*. Incidentally since, I believe, Korshenewsky's ideas have never been verified experimentally, I would suggest to Prof. Palmer that the technique he has developed for the study of current-distribution might be applied to the distribution on open-wire aerials at short wave-lengths. It is to be presumed that the current at points P and P' is in opposite phase to that at Q_1 and Q_1' and this might have been shown in the diagrams by plotting with negative ordinates. In this case the curves would not have been symmetrical about the zero axis, and it would be interesting to know the explanation of the asymmetry in, say, figure 2.

In the first paper the authors have discussed the optimum conditions of a frame when used as a transmitting aerial on very short wave-lengths. Since it has already been shown that the mere measurement of current at a particular point in a frame has little meaning by itself, the important part of this paper is that dealing with conditions of maximum radiation. From this viewpoint the criticism of the work of Walmsley and Bewick at the foot of p. 74 appears to be scarcely justified, for the following reason. In figure 12 the optimum size of frame for maximum radiation is that corresponding to a height of 0.4λ and a width of 0.5λ , while if the height is increased to 0.5λ the radiation field is only reduced by about 25 per cent. Now the optimum sizes of frames found by Walmsley and Bewick are 0.47λ and 0.5λ square in two experiments respectively; yet the authors state in their footnote on p. 74 that no radiation will occur if these conditions are exactly fulfilled. The explanation of the result as being due to the effect of the waves reflected from the earth seems scarcely sufficient, and if it is correct it must always be considered in connexion with such results as those illustrated in figures 4 and 12. Furthermore, frames of the dimensions under consideration will have markedly directional radiation characteristics and these must be taken into account in comparing the measured radiation from frames of different dimensions.

From the radio-communication engineer's point of view the real point at issue here is to know the relative advantages of the so-called "formatized" frame and a suitable antenna array occupying the same spatial dimensions and supplied with the

* N. von Korshenewsky, *Z. f. Technische Physik*, 10, 604 (1929); see also F. M. Colebrook, *J. Inst. E.E.* 71, 235 (1932).

same input power. Does the experience of the authors throw any light on this aspect of the communication problem?

Dr L. E. C. HUGHES. The method of treating antennae of dimensions comparable with the wave-length as given by the authors is particularly interesting and likely to be of great value when applied to the more complicated directional antennae used in practice. A new type of antenna, called the diamond or rhomboid, is being tried out on both sides of the Atlantic. It consists of four wires in a horizontal plane, with the angles of maximum radiation (and also reception) so arranged that the effects are additive along the direction of the longer diagonal and tend to cancel perpendicularly for the four wires taken together. This is based on the principle that the angle of maximum radiation from a non-resonating wire appears to reach a limit of about 70° when the wire is more than about 6 wave-lengths long. A feature of the arrangement is that the termination at the far end of the diamond, the two sides being fed in opposite phases, renders the antenna aperiodic for a wide band of frequencies. The exact mode of operation of this antenna seems to be obscure, but an extension of the work contained in the paper promises a solution.

AUTHORS' reply. Dr Smith-Rose has raised several interesting points. Because the work is necessarily and unavoidably incomplete at the moment, we realize that no such simple theory as that now set forth can completely explain the action of short-wave frame aerials, but it seemed desirable to publish the work as far as it has gone together with the theory as far as it has been developed. In this respect the present communication may be, we fear, almost as unsatisfactory as the earlier publications.

The point P is the point nearest to the radiating source and therefore is the pole of the spherical wave-front when incident on the frame. The vertical component of the electric vector is therefore a maximum at P and not uniform. In the case of a point source located near the centre of the frame, the point P can be made to travel round the frame in a manner which depends on which part of the frame is nearest to the point source. We have not been able to obtain experimentally a perfectly symmetrical case in which an ideal point source is exactly in the centre of a circular or square frame. The point P is also independent of the position of any tuning-condenser which may be in the frame.

Concerning Korshenewsky's work and the recent work of Dr Smith-Rose and his collaborators at the National Physical Laboratory, we originally attacked the current-distribution question from the transmission-line standpoint but felt that the necessity of bending the wires to form a frame led to difficulties at the point of contact owing to the terminal impedance of the lines, and, as the method seemed somewhat artificial when applied to closed frames, we have, at the moment, abandoned it.

The reason for the lack of symmetry about the zero axis in the current-graphs in the second paper, when alternate peaks measured from P' are plotted with negative ordinates, is partly due to inability to measure small currents with a square-law instrument. Probably our minimum current-values were in reality zero in the cases

where the ratio of the wave-length to the frame-perimeter was approximately an integer, whilst the presence of minor Q_1 and Q_1' antinodes round the frame when this ratio was not an integer would account for small currents at the positions of the major current nodes.

Concerning our criticism of Walmsley and Bewick's paper, our objection is not to their experimental values, which approximate closely to our own, but to their conclusions. We do not believe that their maximum currents obtained for $H = W = 0.47\lambda$ and 0.5λ are due to their frame being "the normal 0.5λ square size of frame." We think that the old theory which leads to this conclusion regarding the frame-width is erroneous. When a frame of these dimensions is raised high above the ground, both the frame current and the horizontal radiation from the frame vary and diminish, showing that the ground is responsible for the effect described; whilst, if a frame of dimensions $W = 1.0\lambda$ and $H = 0.4\lambda$ be similarly raised, its circulating current and radiation properties remain practically unaltered. The large permanent oscillations which are set up in a frame for which $H = W = 0.5\lambda$ preclude a large radiation resistance. In our experiments we have been unable to detect any appreciable horizontal radiation when the frame-dimensions were such that permanent oscillations were set up. So far we have only considered horizontal radiation perpendicular to the sides and in the plane of the frame (i.e. the case in which $\gamma = 0^\circ$).

We are in complete agreement with Dr Smith-Rose concerning the desirability of knowing the relative efficiency of a formatized frame and an antenna array; but although we believe a formatized frame may be better than a half-wave dipole with a suitable reflector, we have not yet had time to carry out any experiments on relative efficiencies.

In reply to Dr Hughes: the work to which he refers was, we believe, first carried out in America by E. Bruce*. Mr R. Curry at Hull is now investigating the problem of formatizing triangular frames for reception and transmission, but we have met with considerable difficulty in applying the theory of this paper to frame-wires which are not parallel. We believe that the solution of the triangular frame may throw considerable light on the diamond aerials to which Dr Hughes refers, but the problems are different in that the frames we are studying are closed circuits and do not radiate and receive by virtue of critically terminated open ends.

* *Proc. Inst. Radio Eng.* 19, 1406 (1931).

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THE DIURNAL VARIATION OF THE INTENSITY OF WIRELESS WAVES REFLECTED FROM THE IONOSPHERE

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ABSTRACT. An account is given of the diurnal variation of the relative intensity of waves returned from the ionized regions of the upper atmosphere as observed over the early morning period from about 2 a.m. until about 9 a.m. The relative intensity is taken as the ratio of the intensity of the downcoming wave to that of the ground wave. The influence on the intensity of electron-limitation and of absorption-limitation is discussed, in the light of theoretical ionization curves given by Chapman. The experimental observations described show that the magneto-ionic doubling of the echo, which has been observed by Appleton and Builder for the *F* region, occurs also for the *E* region. The doublet echo for this region is observed only for a short period of the morning, owing to the fact that the extraordinary ray is very soon totally absorbed.

§ 1. INTRODUCTION

ALTHOUGH within the last few years much work has been done in the study of the equivalent height of reflection of wireless waves from the upper atmosphere and in the determination of their polarization on arrival at the ground, the study of the efficiency of reflection has not received corresponding attention. In an early discussion of the factors controlling the intensity of downcoming waves Appleton pointed out that there were two processes that would tend to make the reflection coefficient less than unity. In the first place, owing to collisional friction, the waves may be absorbed in passing through one of the ionized regions, thus suffering what Appleton termed "absorption limitation." Secondly, there may be an insufficient electron-density to cause an appreciable return of the energy, in which case the impaired reflection is due to "electron-limitation." The object of this paper is to consider the relative influence of these two factors in certain practical cases.

On the theoretical side we know, from the simple Lorentz theory of dispersion, that when no impressed magnetic field is operative the effect of absorption-limitation can be expressed in terms of an absorption coefficient k given by

$$k = \frac{\nu}{2c\mu} \cdot \frac{4\pi Ne^2}{m(p^2 + \nu^2)} \quad \dots\dots(1),$$

in such a way that the ratio of the intensity of the emergent wave to that of the incident wave is given by

$$\frac{E}{E_0} = e^{-\int k ds}$$

The refractive index μ in the above expression (1) is given by

$$\mu^2 = 1 - \frac{4\pi N e^2}{m(p^2 + \nu^2)} \quad \dots\dots(2),$$

where

- c is the velocity of light in free space;
- ν the collisional frequency of the electrons in the medium;
- N the number of electrons per cm^3 ;
- e, m the charge and mass of the electron;
- p the angular frequency of the waves.

In this paper the absorption caused by the electronic component of the ionized regions will be discussed. It has definitely been established by Appleton that in the upper or *F* region refraction and absorption are caused chiefly by electrons, and it seems probable that this is also true for the *E* region.

The above relationships are not valid if μ changes rapidly in a distance comparable with the wave-length of the waves in the medium. As a typical example of true absorption we have the case of a wave, reflected from the upper or *F* region, being absorbed in the lower or *E* region through which it must pass.

In terms of Appleton's analysis the waves will be completely refracted downwards when they reach a point where there are sufficient electrons to reduce the refractive index to zero for vertical incidence. It is not, however, a sufficient condition for the complete return of the energy of the waves that μ should be reduced to zero at one level in the ionized region. Hartree has shown for several special cases that the coefficient of reflection depends also upon the total thickness of the region, measured in terms of the free-space wave-length of the waves. The case considered by him which most closely approximates to that of the *E* region is that in which there is a linear decrease of μ^2 to a minimum value μ_m^2 as the height above the earth's surface increases, with a similar increase to $\mu^2 = 1$ for a further increase in height. Excluding absorption and taking the case of the normal incidence of plane waves, the region will reflect only a quarter of the energy for $\mu_m^2 = 0$, even when the thickness is very great compared with the wave-length. A small amount of energy will be reflected before there are sufficient electrons to reduce the refractive index to zero, that is when $\mu_m^2 > 0$. A reflection coefficient nearly equal to unity will be obtained only when there are more than sufficient electrons to reduce μ_m^2 to zero—that is when $\mu_m^2 \geq -0.1$ in terms of equation (2)*. If we suppose that in the earth's atmosphere the variation of the refractive index with height is similar to that chosen by Hartree and that the thickness is great compared with the wave-length, then, as the ionization increases with time of day, a reflected wave of small intensity will be observed before the minimum value of μ^2 is zero. When it is just zero the amplitude of the reflected wave will be about 50 per cent

* It should be noticed that in terms of the original analysis the right-hand side of equation (2) is equal to $c^2 k^2 / p^2$ for negative values if we keep μ^2 only for the positive values in this equation. The use of negative values of μ^2 is a convenient way of expressing the fact that the real value of the refractive index is zero in a certain thickness of the refracting regions.

of that of the incident wave and we shall expect perfect reflection only when μ_m^2 becomes negative and equal to about -0.1 . The amplitude of the reflected wave will be small, on account of this phenomenon of electron-limitation, when during the diurnal variation of the ionization either layer just begins or just ceases to reflect the waves. It must be remembered that electron-limitation and absorption may be effective at the same time.

§ 2. THEORETICAL DISCUSSION

In order to obtain an approximate idea of the cause of the diurnal variation of the relative intensity of the downcoming waves, a possible case is discussed below for which use may be made of the theoretical curves given by Chapman* for the variation of the ionization with height in the atmosphere at various times of the day for latitude 60° . This discussion is confined to the case of the early morning period in summer, when, after sunrise, the ionization begins to increase. The early

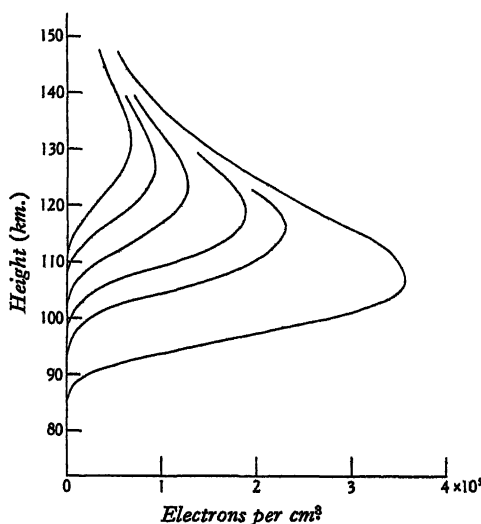


Figure 1. Assumed ionization at 3.36, 4.00, 4.22, 5.00 and 5.54 a.m. and noon.

morning period is of special interest because of the rapid change that takes place in the ionization in consequence of the incidence of the effective solar rays on the atmosphere. The curves of figure 1 show the variation of ionization with height for a midsummer morning. Although they are based on Chapman's curves they differ from them in several minor respects which will be discussed later. These curves correspond to the variation of ionization with height in the *E* region, the actual value of the number of electrons per cm^3 being obtained by assuming that Chapman's value $n/n_0 = 1$ is equivalent to 4×10^5 electrons per cm^3 , the average value given by Appleton and Naismith† for summer in approximately this latitude. The height

* *Proc. Phys. Soc.* 43, 26 (1931).

† *Proc. R.S. A* 137, 36 (1932).

at which the ionization occurs has been adjusted to correspond to that of the *E* region to a first approximation.

In order to calculate the absorption index, the variation of the collisional frequency (ν) of the electrons with height must be known. The values used in this paper are those given by Pedersen*. This variation is shown in figure 2.

Suppose that a spherical wave is sent upwards from a point on the earth's surface and that the downcoming waves are received at a point near the transmitter, so that we are dealing with a case of substantially vertical incidence. The wave-length is chosen to be 100 metres, a wave-length frequently used in the experiments. Owing to the variation of the time of sunrise with height above the ground, region *F* will be first irradiated by the sun and the ionization will begin to increase there before it does so in the *E* region. Since the rate of recombination in

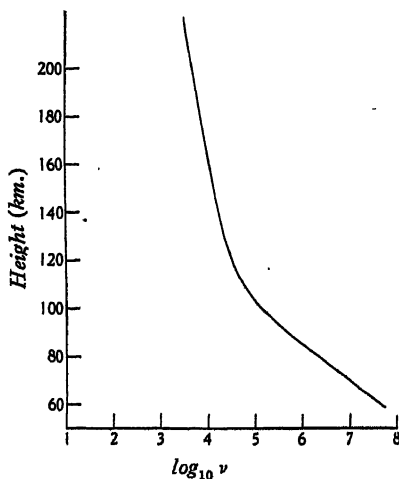


Figure 2.

region *F* is probably low, the ionization will build up fairly rapidly and it is reasonable to suppose that region *F* will be a good reflector for 100-metre waves shortly before sunrise at the *E* region. In the following work it is convenient to compare the intensity of the downcoming wave (denoted by *F*) from the *F* region or (denoted by *E*) from the *E* region with the intensity of the ground wave (denoted by *G*) at the receiver. If we assume that at 2.45 a.m. the *F* region is a good reflector and also that there is little absorption in the *E* region, then at this time we may take the ratio *F*/*G* to be unity. The ratio *F*/*G* or *E*/*G* at other times of day may then be compared with *F*/*G* at 2.45 a.m.

Appleton and Ratcliffe have previously shown that the total absorption suffered by the waves in their atmospheric path may be found by measuring the "reflection coefficient of the ionized regions." This quantity ρ is so defined that it is equal to $\alpha F d_1 / G d_0$, where *F* and *G* are as defined above, while d_1 and d_0 are the distances

* *The Propagation of Radio Waves* (Copenhagen). The values of ν used above are those given by Pedersen for the atmosphere which he has called "atmosphere *F*."

travelled by the atmospheric and ground waves respectively. The constant α depends upon the radiation characteristics of the transmitting aerial and upon the attenuation of the ground wave. In the experimental work described below α could not be determined, so that relative values of the ratio F/G or of E/G have been measured.

At later times of day, irradiation of the E region will cause the ionization shown in figure 1. The first effect of the increase of ionization in the E region will be to interpose an absorbing region in the path of the waves reflected from the F region. Since such waves pass twice through this absorbing zone, the total absorption will be $2\int kds$, the integral being evaluated for the total thickness of the E region. At

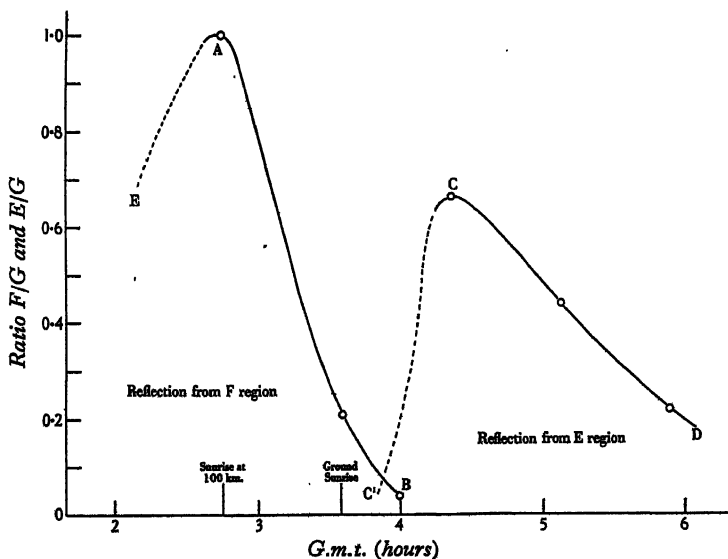


Figure 3.

times later than 2.45 a.m., therefore, the ratio F/G will be reduced from unity to $e^{-2\int kds}$. This ratio has been calculated by means of the formula

$$k = \frac{\nu}{2\mu c} \frac{4\pi N e^2}{m p^2} \quad (p^2 \gg \nu^2)$$

by graphical methods for the times 3.36 and 4.00 a.m. The results of the calculation are shown in the curve of figure 3 from A to B .

The number N_0 of electrons required to reduce the refractive index to zero, for 100-metre waves, is from equation (2) given by

$$N_0 = \frac{m p^2}{4\pi e^2} = 1.115 \times 10^5 \text{ per cm}^3 \quad (p^2 \gg \nu^2).$$

By 4.22 a.m. there are sufficient electrons in the E region to cause the return of these waves, so that at some time between 4.00 and 4.22 a.m. the waves will be intercepted by the E region and returned from it. Since we are considering spherical waves, account must be taken of the fact that when they are returned from the

E region the distance of travel is approximately half that for the *F* region. Thus at 4.22 a.m. we shall have $E/G = 2$ for no absorption. Taking into account the absorption in the lower half of the *E* region the ratio becomes $2e^{-2\int kds}$. In considering the absorption of the waves in the lower part of the reflecting *E* region we must remember that the waves travel into the region until they reach a point where there are sufficient electrons to reduce the refractive index to zero. At this point the index of absorption k becomes infinite, and the question arises whether this simple theory is inadequate in that it gives infinite absorption for such a reflection. That it does not do so can be seen by examining the absorption for the two cases in which the ionization increases linearly and parabolically with height.

Suppose that at a height h_0 above the earth's surface the number of electrons per cubic centimetre begins to increase and does so according to the equation $N = N_0 y/y_0$, where y is the distance measured above h_0 . For N_0 it is best to choose the value $N_0 = mp^2/4\pi e^2$ so that y_0 is the actual distance travelled by the waves in the ionized region. Then

$$\mu^2 = 1 - y/y_0.$$

To evaluate $2\int kds$ we have therefore

$$\begin{aligned} 2\int kds &= \frac{1}{c} \int_0^{y_0} \nu \frac{1 - \mu^2}{\mu} dy \\ &= -\frac{2y_0}{c} \int_1^0 \nu (1 - \mu^2) d\mu \end{aligned} \quad \dots\dots(3),$$

where ν is a function of y and therefore of μ . Although the index k becomes infinite at $y = y_0$ the total absorption is finite.

If, above h_0 , N increases according to the equation $N = N_0 y^2/y_0^2$, where $N_0 = mp^2/4\pi e^2$ and y_0 is the actual distance travelled by the waves in the region as before, then we have $\mu^2 = 1 - y^2/y_0^2$ and

$$\begin{aligned} 2\int kds &= \frac{1}{c} \int_0^{y_0} \nu \frac{1 - \mu^2}{\mu} dy \\ &= -\frac{y_0}{c} \int_1^0 \nu (1 - \mu^2)^{\frac{1}{2}} d\mu \end{aligned} \quad \dots\dots(4).$$

Thus in both cases the total absorption is finite.

An examination of the curves of figure 1 shows that the ionization follows very closely a parabolic distribution up to the value $N_0 = 1.115 \times 10^5$ electrons per cm.³ The absorption of the waves in the lower part of the *E* region has therefore been calculated by the aid of equation (4), the integral being evaluated graphically for the times 4.22, 5.00, 5.54 a.m. and noon. The corresponding values for $E/G = 2e^{-2\int kds}$ are shown in figure 3 from *C* to *D*.

There is at present no theoretical analysis describing the effect of the thickness of the refracting region on the coefficient of reflection for spherical waves. We may, however, roughly estimate the effect of electron-limitation on the relative intensity of waves refracted from the *E* region by reference to the results of Hartree for plane waves. Since $\mu^2 \propto N$ we can see from figure 1 that μ^2 will decrease to a

minimum (at the maximum value of N) and then increase again as the height is increased, in a manner similar to the triangular variation of the square of the refractive index with height chosen by Hartree. The total thickness of the region is always great compared with the wave-length. We should expect therefore that at 4.22 a.m. the effect of electron-limitation will be negligible but that between this time and 4.00 a.m. it will be of increasing importance. It is probable therefore that the relative intensity of the waves returned from the E region will increase from a small value at about 4.00 a.m. to the value shown in figure 3 at 4.22 a.m. This increase has been indicated by the dotted line in that figure ($C'-C$).

Figure 3 gives now the diurnal variation of the relative intensity of the waves from a time just before sunrise until well into the morning. The waves are at first returned from the F region with maximum relative intensity. Their intensity decreases rapidly as time advances owing to absorption in the E region where the ionization is building up. At about 4.00 a.m. there is nearly sufficient ionization in the E region to cause the waves to be returned from that region. The E reflection increases in intensity owing to the disappearance of electron-limitation until 4.22 a.m., when the waves from the E region have their maximum relative intensity. After this time the relative intensity of these waves decreases owing to absorption in the lower part of the E region itself. The above discussion has attributed all the absorption to the E region. It is perhaps permissible to do this, for the collisional frequency of the electrons in the E region is of the order of 100 times that for the F region, so that for the same ionization the absorption index will be also about 100 times greater.

We must now try to decide on the cause of the variations in the intensity of the waves reflected from F region before 2.45 a.m. After sunset on the previous day the ionization in regions E and F begins to decrease, with the result that the reflection of a 100-metre wave from region E and ultimately from region F may cease and no reflected wave be observed at the ground. When the influence of the sun is once again felt in region F the ionization increases again, and taking into account the electron-limitation effect in that region, we should observe first a small signal, which increases in intensity as the region becomes more perfectly reflecting. This has been indicated in the dotted portion of figure 3 from E to A . Reflection from the F region will cease during the night only if the maximum number of electrons decreases to a value less than the critical value $N_0 = mp^2/4\pi e^2$. If reflection from region F persists throughout the night we should expect the waves to have a steadily increasing intensity, owing to the continual removal of the absorbing E region.

§ 3. THE EARTH'S MAGNETIC FIELD

From the Lorentz theory we know that if there is an impressed magnetic field operative in the region of ionization, then the motion of the electrons is influenced by it in such a way that the refractive index and the absorption coefficient are functions of the intensity of the field. The analysis of the magneto-ionic theory of

propagation of a wave, in any direction with respect to the applied field, has been given by Appleton in previous papers*. On the assumption that the frequency of the wave is greater than the frequency of collision ν of the electrons he has shown that

$$\mu^2 = 1 - \frac{2x(1-x)}{2(1-x) - y_T^2 \mp \sqrt{\{y_T^4 + 4y_L^2(1-x)^2\}}}$$

and

$$k = \frac{(1-\mu^2)^2}{2c\mu} \cdot \frac{\nu}{x} \left[1 + \frac{y_T^2}{2(1-x)^2} \mp \frac{y_T^4}{2(1-x)^2 \sqrt{\{y_T^4 + 4y_L^2(1-x)^2\}}} \right],$$

where

$$x = \frac{4\pi Ne^2}{m\bar{p}^2}, \quad y_L = \frac{H_L e}{mc\bar{p}}, \quad y_T = \frac{H_T e}{mc\bar{p}},$$

and H_L and H_T are the components of the earth's magnetic field along and perpendicular to the wave normal.

For vertical incidence of 100-metre waves in London we have $y_L = 0.406$ and $y_T = 0.174$, so that

$$\mu^2 = 1 - \frac{2x(1-x)}{2(1-x) - 0.0303 \mp \sqrt{\{0.00092 + 0.66(1-x)^2\}}}$$

and

$$k = \frac{(1-\mu^2)^2}{2c\mu} \cdot \frac{\nu}{x} \left[1 + \frac{0.0303}{2(1-x)^2} \mp \frac{0.00092}{2(1-x)^2 \sqrt{\{0.00092 + 0.66(1-x)^2\}}} \right].$$

The transverse component of the applied field exerts little influence on the refractive index and on the absorption coefficient except in the region where $x \approx 1$.

In order to obtain an approximate idea of the diurnal variation of the relative intensity when a magnetic field is operative, the data for the ionization in the E region and for the collisional frequency ν of the electrons given in the previous sections have been used for calculations of the relative intensity for the case of propagation entirely along the field. The intensity of the longitudinal component of the applied field has been taken equal to the vertical component of the earth's magnetic field in London. Thus $y_L = 0.406$. For such a case the expressions for the refractive index and for the absorption coefficient are simpler than for the general case. They are

$$\mu^2 = 1 - \frac{x}{(1 \mp y_L)}$$

and

$$k = \frac{(1-\mu^2)}{2c\mu} \cdot \frac{\nu}{(1 \mp y_L)}.$$

The lower sign in these equations refers to the ordinary ray and the upper to the extraordinary ray.

Before the waves are returned from the E region they must pass twice through this region when returned from the F region. The absorption suffered in the E region is then given by

$$2 \int k ds = \frac{1}{c(1 \mp y_L)} \int \frac{\nu(1-\mu^2)}{\mu} ds,$$

* *J. Inst. E.E.* 71, 642 (1932).

integrated through the total thickness of region E . When they are returned from the E region the waves penetrate a distance y_0 into the region to the point where $\mu^2 = 0$ and return from this point. The total absorption suffered is then

$$= \frac{1}{c(1 \mp y_L)} \int_0^{y_0} \nu \frac{1 - \mu^2}{\mu} dy.$$

For a parabolic distribution of the ionization

$$N = N_0 y^2 / y_0^2 \text{ with } N_0 = \frac{m p^2}{4\pi e^2} (1 \pm y_L).$$

This becomes

$$\frac{y_0}{c(1 \mp y_L)} \int_1^0 \nu (1 - \mu^2)^{\frac{3}{2}} d\mu.$$

It should be noticed that the ordinary ray travels a greater distance y_0 in the region than does the extraordinary ray.

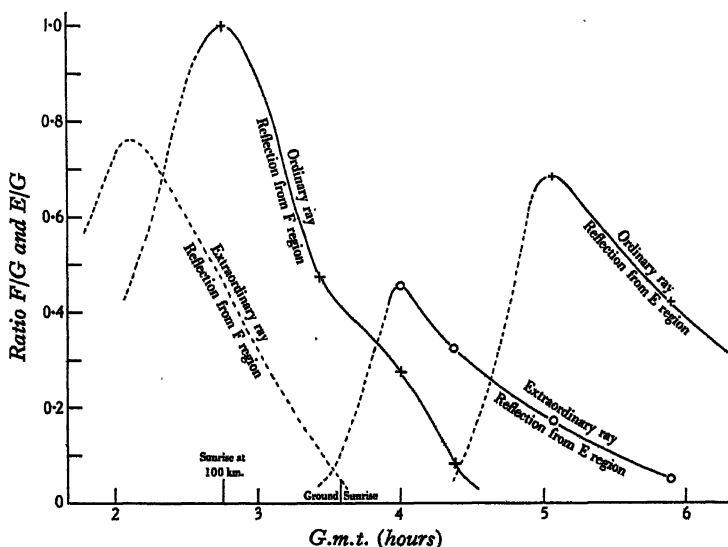


Figure 4. o Extraordinary ray. + Ordinary ray.

Assuming that at 2.45 a.m. the ordinary ray is returned from the F region and suffers very little absorption, so that the ratio F (ordinary)/ G may be put equal to unity at this time, the diurnal variation of the relative intensity shown in figure 4 is found as a result of these calculations.

With the applied magnetic field operative, the additional features to be looked for in the diurnal variation of the relative intensity are as follows. Before the E region becomes sufficiently ionized, two components of the waves returned from the F region will be received at the ground. With the beginning of ionization in the E region both components will be absorbed, the extraordinary ray suffering the greater absorption. Since fewer electrons are required to cause the return of the extraordinary ray, this component will be first returned from the E region, the ordinary ray being returned at a later time. When either component is first returned

the electron-limitation effect will cause it to have small intensity, but as time advances each component will exhibit a maximum of intensity owing to the decreasing effect of electron-limitation together with increasing absorption in the lower part of the *E* region. In spite of the fact that the ordinary ray, when reflected from the *E* region, travels a greater distance in the ionized medium, the absorption for this ray is less than that for the extraordinary ray.

In Chapman's calculations of the ionization it is assumed that a monochromatic radiation from the sun is absorbed in an atmosphere in which the density varies exponentially with height. If the number of ions produced per second is *I* it is also assumed that the ionization condition is of the form

$$dn/dt = I - \alpha n^2,$$

n being the total number of ions per cm.³ at any time. The recombination coefficient α is taken to be constant for all heights. From these considerations it appears that as a result of the ionization during one day a considerable amount of ionization will remain, after sunset and throughout the night, at the lowest levels reached by the ionization at noon. In figure 1, for instance, the curve for 4 a.m. should not according to Chapman show zero ionization at about 108 km. but should show a small but appreciable amount down to about 85 km. In the above work this residual ionization has been arbitrarily neglected by terminating the curves at a greater height. If the residual ionization at low levels does exist it will introduce, throughout the night, a considerable amount of absorption into the path of the waves reflected from *F* region. This is contrary to experimental observations, for the intensity of the *F* reflections is always high during the night, except at those times when it is obvious that electron-limitation in this region is effective.

§ 4. EXPERIMENTAL INVESTIGATION

In the series of experiments presented below, observations have been made of the relative intensity of the reflected wave with respect to the ground wave over a period extending from midnight until some time after sunrise at the ground. Wave-lengths from 100 to 170 metres have been used. In the first experiments the frequency-change method of observing the effective height has been employed. The average value of the relative signal-strength may be arrived at from the photographic records obtained, either by observing the fading or from the fringes that result when the frequency is changed. Fading may occur owing either to actual intensity-variations of the downcoming wave or to interference between the downcoming wave and the ground wave. The short-period fading that causes the signal to vary between maximum and minimum many times in the course of a minute is probably of the interference type, the maximum occurring when the downcoming wave and the ground wave are in phase and the minimum when they are in antiphase. For the former the total signal may be represented by the sum of the intensity *F* of the downcoming wave and that *G* of the ground wave, while in the latter case we have (*F* - *G*). If the observed ratio (*F* - *G*)/(*F* + *G*) = *x*, then *F*/*G* = (*x* + 1)/(1 - *x*). When a frequency-change is made we purposely bring the

two waves into and out of phase so that the same ratio may be measured. In these experiments the amplifier was calibrated by means of a local oscillator.

The frequency-change method suffers from the disadvantage that when there is more than one downcoming wave the records are complex and it is difficult to sort out the various components. For this reason the Breit and Tuve method, as developed by Appleton and Builder, has been employed in the later runs. With this method the various components are received separately and their relative intensity may be easily measured. It is now well known that the magneto-ionic components of waves of the order of 100 metres return to the earth circularly polarized owing to the influence of the earth's magnetic field on the motion of the electrons in the ionized regions, the extraordinary ray having a right-handed sense of rotation and the ordinary component a left-handed sense, as looked at along the ray in the direction in which the wave is travelling. When the frequency-change method was used and the signals were received on an aerial or on a loop no account was taken of this fact, so that for these results it is the average maximum value of the two components together that has been measured. With the echo method, signals being received on an ordinary loop aerial, the same thing is measured when the two components are not resolved by the layer and the apparatus, but when they are so resolved the average maximum value of each component may be found separately. If, however, a circularly polarized aerial, which will receive the left-handed circularly polarized component to the exclusion of the right-handed component or vice versa, is used, then the average maximum value of each component may always be found if the waves are truly circularly polarized. I am greatly indebted to Messrs Ratcliffe and E. L. C. White for advanced details of this aerial, which has later been described in a paper published in the *Philosophical Magazine**.

§ 5. EXPERIMENTAL RESULTS

Several experimental runs are described and discussed below.

February 12, 1932. Wave-length 170 metres. The frequency-change method was used in this run, the relative intensity being deduced both from the fringes and from the fading with good agreement. The results are shown in figure 5. The

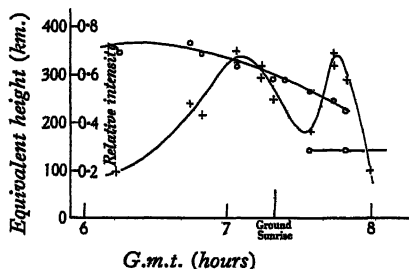


Figure 5. Wave-length 170 metres, February 12, 1932.
+ Relative intensity. O Equivalent height.

* *Phil. Mag.* 16, 125 (1933).

wave from *F* region was observed just after 6 a.m., its amplitude being then small. Between 6 a.m. and 7 a.m. the amplitude steadily increased. Since it is improbable that an hour would be required for the electron-density to build up to the fully reflecting value in the *F* region, we may account for some, at least, of this increase by the continued removal of absorption in region *E*. After 7.05 a.m. a sharp decrease in the intensity was observed, this being due to the increase of ionization and therefore absorption in region *E*. This decrease continued until 7.35 a.m., after which time another maximum of the relative intensity was observed. This coincides with the transition from *F* to *E* reflection. Twenty minutes later the intensity of the wave reflected from region *E* had decreased to a small value owing to absorption in the lower part of this region. This set of results is typical of the results obtained with the frequency-change method.

June 22, 1932. Wave-length 100 metres. In this run the echo method was used, the signals being received on a loop aerial. In figure 6 (a) the relative intensities

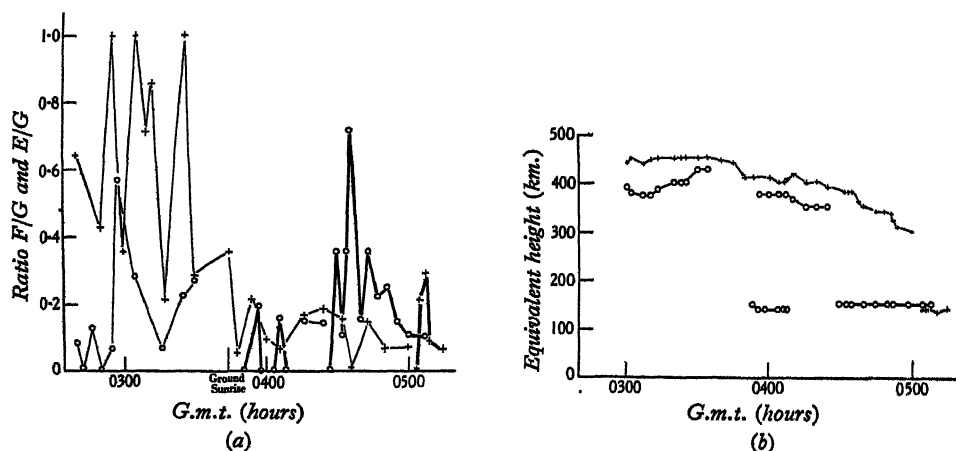


Figure 6. June 22, 1932. Wave-length 100 metres*.

* In this and in the following figures the cross is used for the ordinary ray and the circle for the extraordinary ray. The thin line is used for reflections from *F* region and the thick line for reflections from *E* region.

are shown and in figure 6 (b) the corresponding equivalent heights of reflection. Before 3.30 a.m. the waves reflected from the *F* region show a considerable amount of intensity-fading. Reflection from the *F* region had persisted throughout the night, the ordinary ray being stronger than the extraordinary ray. Just before ground sunrise the intensity of both components reflected from region *F* begins to decrease owing to the beginning of absorption in region *E*, and this continues until after the appearance of reflections from region *E* itself. About 4 a.m. a weak reflection is obtained from region *E*, but this echo does not give maximum intensity until 4.40 a.m. This is the extraordinary ray for region *E*, its appearance coinciding with the disappearance of this component from the *F* region; there is actually a disappearance of the echo between 4.10 a.m. and 4.30 a.m. After the maximum

there follows a decrease in the intensity which continues until 5.10 a.m. At 5.05 a.m. a doublet echo is obtained from the *E* region, figure 7, the more retarded component showing a small maximum (the ordinary ray). After this time the records are

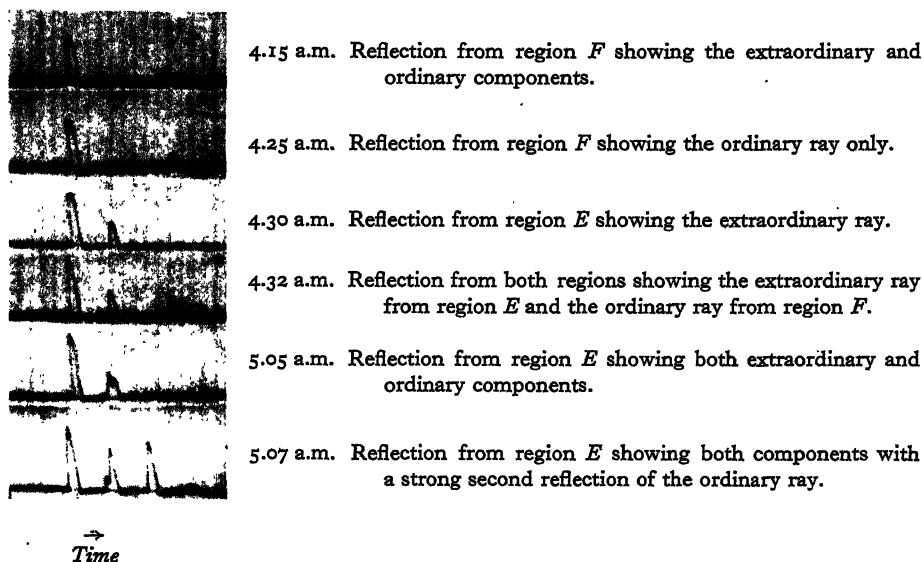


Figure 7. June 22, 1932.

obscured by interference, but there is no doubt that this latter component is the ordinary ray for the *E* region.

June 17, 1932. Wave-length 98 metres. Reception on a loop aerial. This set of results, figures 8 (*a*) and 8 (*b*), will serve to amplify those of the previous run. During the night, from 1 a.m. until 3.20 a.m., the ordinary ray from the *F* region appeared only occasionally. This is most certainly due to the fact that while the *F* region was a good reflector for the extraordinary ray, the electron-limitation effect caused it to be a very poor reflector for the ordinary ray. At 3.30 a.m. conditions improved for the ordinary ray, but since both components of the doublet were almost superimposed it is not possible to estimate their relative intensity separately. The difference in the equivalent height can, however, be approximately obtained. The total intensity decreased steadily until 4.15 a.m., at which time we observe the first reflection from the *E* region, the extraordinary ray. At 5 a.m. the ordinary ray from the *E* region is observed. In this set of results the maximum for both components is seen*.

* In the two runs described immediately above, the polarization of the downcoming waves was not observed. For the *F*-region reflections there is no doubt about the identity of the two reflected components, the ordinary and the extraordinary rays. The identity of these two components in the *E*-region reflections was for these two runs worked out from the variation of the intensity with time of day and from the fact that a doublet echo was obtained for this region. It seemed desirable to make certain of these facts by using a polarized aerial with which the polarizations of the two components from the *E* region could be found. Such a run has been carried out with a wave-length of 100 metres. Precisely similar results to those described above were obtained.

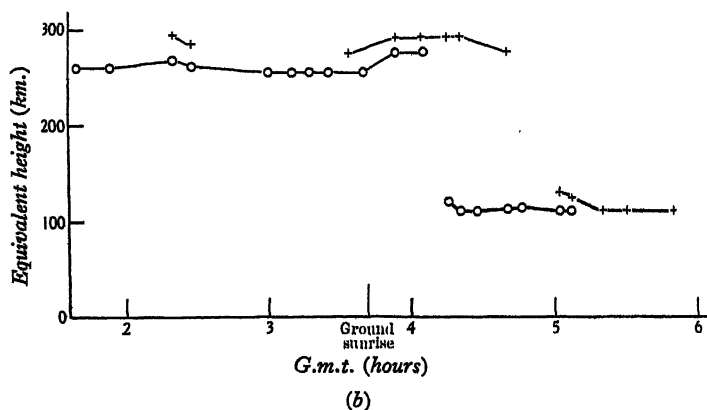
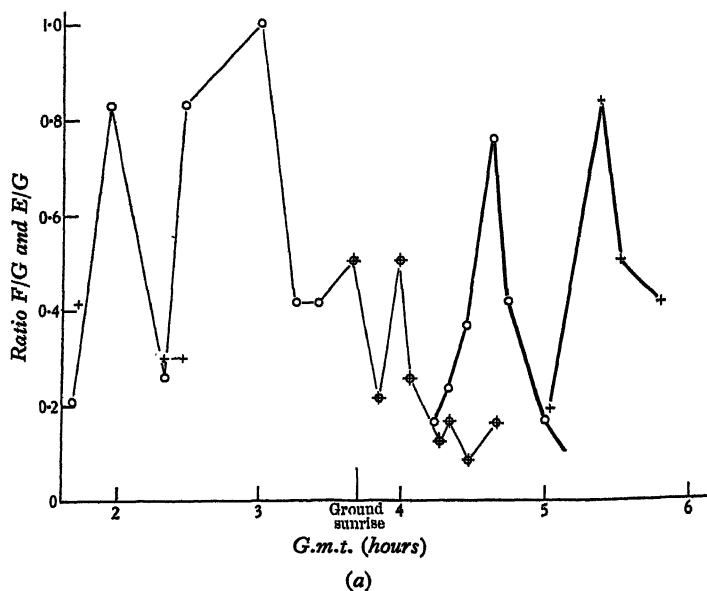


Figure 8. June 17, 1932. Wave-length 98 metres.

March 25, 1933. Wave-length 100 metres. Reception on a circularly polarized aerial. These results, figures 9 (a) and 9 (b), show very clearly the electron-limitation effect in the *F* region and the ultimate absorption of the waves by region *E*. Transition from *F* to *E* reflection was observed, but on this day the ionization in region *E* was never sufficiently great for this region to return a strong signal. The first reflection from *F* occurred at about the time of ground sunrise; see figure 9. At 5.54 a.m. a signal of small amplitude, the extraordinary ray, was received. The amplitude increased to a maximum by 6.13 a.m. owing to the removal of the electron-limitation, and a consequent increase in the reflection coefficient for this ray. Since this occurred after ground sunrise, ionization in *E* had already started,

so that the subsequent decrease in the intensity of the extraordinary ray must be accounted for by absorption in region *E*. When, at 6.20 a.m., the *F* region begins to reflect the ordinary ray, we observe an increase in its amplitude, in spite of the presence of absorption in *E* region, as the layer becomes a more and more efficient reflector. The absorption of this ray ultimately follows between 6.46 and 7.20 a.m.

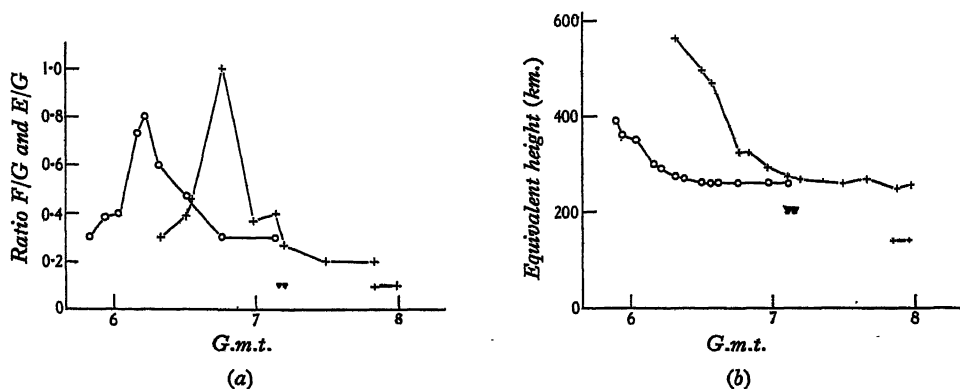


Figure 9. March 25, 1933. Wave-length 100 metres.

At 7.07 a.m. the two components are reflected at very nearly the same height, and at later times the extraordinary ray is absent, presumably completely absorbed in region *E*. At 7.50 a.m. a weak signal was observed from the *E* region, and by that time the relative intensity of the ordinary ray from *F* had been reduced to 0.2. During the period from 6.40 to 7.10 a.m. when the *F* region was a good reflector for both components, the ordinary ray was less absorbed than the extraordinary ray.

§ 6. DISCUSSION OF RESULTS

In the light of the theoretical and practical results we may summarize the general features of the diurnal variation of the relative intensity.

(1) During the night, when the ionization in *E* is small and decreasing, we have two conditions for short waves. (a) *With a wave-length that does not penetrate F region.* A strong signal which steadily increases as the *E*-region absorption is removed will be received, the ordinary ray being the stronger if there is no electron-limitation effect in the *F* region. A wave-length may be found for which the *F* region is a good reflector for the extraordinary ray but, owing to the fact that more electrons are required for the ordinary ray, this ray may suffer electron-limitation. In such a case the extraordinary ray will be the stronger. (b) *With a wave-length that does penetrate F region.* As the ionization in region *F* increases with the incidence of sunlight on the layer, the extraordinary ray is first reflected with a small intensity. Its intensity immediately begins to increase owing to the removal of electron-limitation for this ray. At a later time the ordinary ray is reflected and its intensity also increases for a similar reason.

(2) As the ionization in region *E* builds up, the first effect of the renewed

ionization in this region is to cause increased absorption of the waves which, being reflected from region *F*, pass twice through region *E*. Under these conditions the extraordinary ray is then absorbed more than the ordinary ray.

(3) When the ionization in the *E* region has increased sufficiently this region begins to reflect. The extraordinary ray is first reflected. It is found that the ordinary ray is not reflected until about an hour later. The intensity of each of these components is limited by electron-limitation when it first appears and by absorption at a later time, the absorption taking place in the lower part of the *E* region itself.

§ 7. THE DOUBLET ECHO FROM REGION *E*

In 1931 Appleton and Builder* pointed out that the doublet echo that they had obtained when a single impulse was reflected by the *F* region could be accounted for on the magnetic-ionic theory if the equivalent height as measured by the ordinary ray was different from that measured by the extraordinary ray. This explanation of the phenomenon, which occurs very frequently in the case of reflection from the *F* region, has received ample confirmation since that time. It has since been shown by Ratcliffe and E. L. G. White† that both the extraordinary and the ordinary ray are distinguishable by means of a suitably polarized aerial in reflections from the *E* region at certain times of day, but that the equivalent height of this region as measured by either component is the same.

On several occasions during the course of the work described above, doubling of the echo from the *E* region was observed. The separation of the components was always small. These observations have since been confirmed by some recent work of Appleton‡. It has been found that the intensity of the extraordinary ray from the *E* region is comparable with that of the ordinary ray for only a very short period during the morning, for wave-lengths of about 100 metres, and that this component is probably absorbed during the greater part of the day. This may in some part account for the fact that the doubling of the echo from the *E* region is very infrequently observed.

§ 8. ACKNOWLEDGMENT

I wish to express my thanks to Prof. E. V. Appleton for his encouragement and help in this work.

* *Proc. Phys. Soc.* 44, 76 (1932).

† *Phil. Mag.* 16, 125 (1933).

‡ *Proc. Phys. Soc.* 45, 673 (1933).

551.51.053.5:621.396.11

SOME AUTOMATIC RECORDS OF WIRELESS WAVES REFLECTED FROM THE IONOSPHERE

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AND

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ABSTRACT. Some automatic records of wireless waves reflected from the ionosphere are discussed. The records extend over a period of fourteen months. They indicate that the region below the *F* region may be triply stratified and consist of the intermediate region (effective height approximately 120 to 180 km.), the *E* region (effective height approximately 100 to 120 km.) and the *e* region with an effective height which is always nearly 105 km., within ± 5 km. The *e* region is shown to be intermittent in its occurrence, and is identified with the "nocturnal *E* region" mentioned in previous papers. The temporal variation of the ionization in these three regions is discussed.

A statistical investigation is made to see whether the occurrence of the nocturnal ionization in region *e* is associated with the occurrence of magnetic disturbances or of thunderstorms. It is shown that if the nocturnal ionization was unrelated to magnetic disturbances the probability of the observed coincidences between the occurrence of the two phenomena would be 0.01, and if thunderstorms and the nocturnal ionization were unrelated the corresponding probability would be 0.0015.

§ 1. INTRODUCTION

IN a recent paper⁽¹⁾ we have described an apparatus for continuous automatic recording of the equivalent height of wireless echoes returned from the ionosphere, and have given a preliminary account of some of the results obtained. This apparatus has now been in use for fourteen months, and the present paper gives a fuller account of various conclusions we have been able to draw from the data obtained during this period. We have used the apparatus to make weekly records on the international days of the polar year for the Radio Research Board, and have therefore worked, very largely, on the polar-year wave-lengths of 75 and 150 m.

§ 2. FINE STRUCTURE OF THE IONOSPHERE

It was mentioned in the previous paper that, on a wave-length of 100 m. in the summer months, the normal behaviour is for the *F*-region reflection to give place to the *E*-region reflection discontinuously near sunrise; but that later in the year, with a wave-length of 175 m., cases had been observed in which the transition from the *F* to the *E* reflection took place gradually. Further records have shown that this type of behaviour is quite common, and have led to the recognition of

more than two ionized regions in the ionosphere*. The record reproduced in figure 1 illustrates the phenomenon. This record was taken on November 27, 1932 with a wave-length of 150 m. From 0700 to 0840 an *F* echo was recorded, with equivalent height decreasing from 300 to 200 km. From 0840 to 0940 reflection took place from an intermediate region with variable equivalent height of the order of 180 km., and at 0940 reflection from the *E* region at 130 km. was established. At 1410 on the following evening the intermediate region (150 km.) appeared and at 1510 it gave place to the *F* region (220 km.). The record of figure 2 was taken on the previous evening, November 26, on the same wave-length; it shows a similar behaviour, and, in particular, it shows a great equivalent height for the *F* echo just as it comes in. This is a characteristic behaviour of the *F* echo when the intermediate region is present, and may often lead to the detection of the intermediate region on a record; it is presumably due to group retardation in the intermediate region. The presence of the echo at 1410–1430 will be discussed later. The intermediate region has only been observed, on these wave-lengths, near sunrise and sunset; in the middle of the day the ionization of the *E* region is sufficiently intense to prevent the waves from reaching the intermediate region.

During the winter months the equivalent height of the *E* region on a wave-length of 150 m. is somewhat variable, but lies round about 125–140 km. On a wave-length of 200 m. it is lower, at about 105 km. The high value and the variability on the 150 m. wave-length suggest that this is near the critical wave-length during the winter day, in agreement with the critical-wave-length curve of Appleton and Naismith⁽²⁾. In the summer months the equivalent height of the *E* region ($\lambda = 150$ m.) is less, and of the order of 105 km., and is less variable during the day; moreover the same equivalent height is recorded for a wave-length of 75 m. This seems to show that 150 m. is not near the critical wave-length in the summer.

In the previous paper attention was drawn to the occurrence of nocturnal increases in the ionization of the *E* region. It is now found that the equivalent height of this nocturnal *E* region is remarkably constant from night to night, being about 105 km., whichever wave-length (150 m. or 75 m.) is used. It is found, during the winter months, that daytime echoes may occur sporadically for an hour or two, at any time of day, at the same equivalent height of 105 km. It is very probable that these are due to the type of intermittent ionizing agency which produces the nocturnal *E* region. The echoes in figure 2 between 1410 and 1430 and after 1600 are at an equivalent height of 105 km. (compare the *E*-region height of 130 km. on the same record) and are of this type. Other examples are shown in figure 3† (January 29, 1933) and in figure 4 (December 22, 1932). In the latter figure the 105 km. nocturnal region is present during the sunrise period.

* The presence of more than two ionized regions has also been suggested by Schafer and Goodall⁽¹¹⁾ and Appleton⁽¹²⁾. Our present picture of the detailed structure of the ionosphere corresponds very closely with that suggested by the latter author at a recent discussion before the Royal Society.

† In making the records of figures 3, 7 and 8 a circularly polarized receiver was employed which was automatically switched so as to receive right- and left-handed polarized waves alternately⁽⁶⁾. A black line at the top of the record corresponds to reception of right-handed polarization.

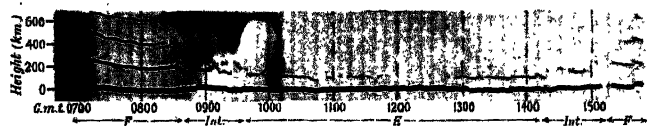


Figure 1. November 27, 1932 (150 m.).

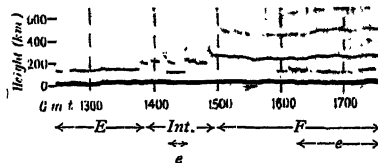


Figure 2. November 26, 1932 (150 m.).

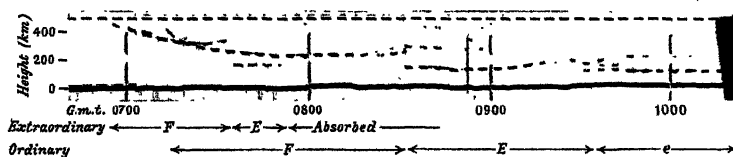


Figure 3. January 29, 1933.

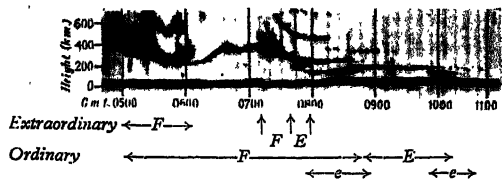


Figure 4. December 22, 1932 (150 m.).

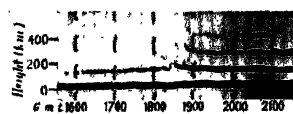


Figure 5. July 7, 1933 (150 m.).

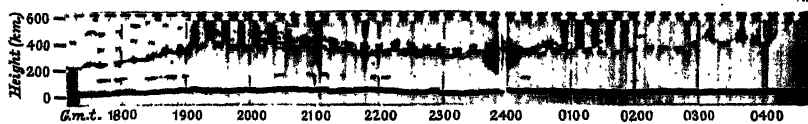


Figure 7. January 26-27, 1932 (150 m.).



Figure 8. March 22, 1933 (75 m.).

During the summer months the *E* region itself appears, on these wave-lengths of 150 and 75 m., at an equivalent height of about 105 km. and, in consequence, the appearance of extra ionization at this level during the daytime owing to the action of the intermittent ionizing agency passes unnoticed. It is occasionally found, however, that a break occurs in the record of the 105 km. echo, of such a nature as to suggest that the reflection has changed from one level of ionization to another extremely near it. Thus at 1830 in figure 5 (July 7, 1933) there is a break in the record, and the echo then seems to descend rapidly from a greater height to the same level as previously. The phenomenon is repeated at 1845; the faint second-order reflection shows the splitting more clearly. This is very suggestive of a jump from a lower to a higher region, accompanied by a group-retardation effect and a magneto-ionic splitting. The same phenomenon occurred at the same time on eight out of nine records made between July 7 and 18, and on the remaining record (July 10) the *E*-region echo gave place to the *F*-region echo in the usual way (possibly with a little intermediate region in evidence) at this same time, 1830. This seems to confirm the idea that in the summer the true *E* region and the intermittent region are practically coincident.

It seems very probable that the nocturnal *E* region and the intermittent daytime region at 105 km. are due to the same ionizing agency, for they both occur at the same level and are both intermittent in character; it is therefore convenient, following Appleton⁽⁴⁾, to give both these the name of *region e*. The possibility of the ionization of region *e* being due to charged corpuscles from the sun, or to thunder-clouds, is discussed in § 4.

In a preliminary account of these results which was contributed by one of the present authors to a discussion at the Royal Society⁽⁷⁾, and in a letter to *Nature*⁽¹³⁾ in which figure 3 was reproduced, the region at a level of 125–140 km. in winter ($\lambda = 150$ m.) was wrongly interpreted as being the intermediate region. The study of records of the type reproduced in figures 1 and 2 has now shown that this is the *E* region and that the intermediate region is above it and region *e* below it, so that there may be a triple stratification of the region between effective heights of 100 km. and 200 km.

The multiplicity of echoes which is possible from the *E* region, the intermediate region, and the intermittent region *e*, makes it very necessary to be cautious in interpreting split echoes from these levels as due to magneto-ionic effects.

A record obtained on December 14–15, 1932 throws some interesting light on the relation between region *E* and region *F*. During the night of December 14 the *F* ionization was very weak, as is evidenced by the fact that, with a wave-length of 150 m., the extraordinary component of the echo was absent, owing to electron-limitation, for five hours, whereas on other days of this month it was never absent during the night. On the following day reflections from the *F* region alone were visible, the *E* region and the intermediate region being too weak to give rise to reflection. It therefore appears that weak ionization in the *F* region is associated with weak ionization in both the *E* region and the intermediate region, and it is reasonable to assume that the ionizations of these three regions are due to a common

cause. This agrees with Appleton's suggestion that all are due to the effect of ultra-violet light.

§ 3. BEHAVIOUR OF THE *F* REGION

By observing the time at which the waves cease to be reflected from the *F* region we know the time at which the ionization-density has decreased to a certain fixed value. These times are plotted throughout the year for a wave-length of 75 m., for the ordinary and the extraordinary wave separately, in figure 6; the times at which the *F* region begins to reflect in the morning are shown also. On this same figure the times of sunset and sunrise both at the ground and at a height of 200 km. are plotted. In computing the times for 200 km., allowance is made for the fact that the obliquity of the sun's rays varies throughout the year*. It is seen that in summer the ordinary wave begins to be reflected about $1\frac{1}{2}$ or 2 hours after ground sunrise, whereas in winter reflection begins about $\frac{1}{2}$ hour after ground sunrise.

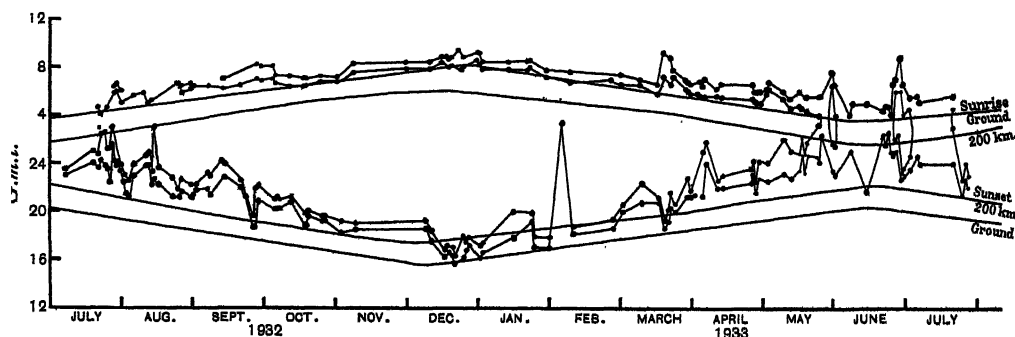


Figure 6.

The effect is noticeable on a similar curve published by Elias, von Lindern and de Vries⁽⁸⁾; they do not, however, comment on it. The phenomenon is very unexpected; we should anticipate just the opposite in view of the fact that the amount of ionization remaining through the night must be considerably greater in summer than in winter. A possible, though improbable, explanation is that the earth is nearer the sun at midwinter than at midsummer, so that the intensity of the sun's light is greater by about 6 per cent.

The records on a wave-length of 150 m., during the winter months when this wave-length is nearly critical, reveal a marked tendency for *F* ionization to increase in density round about midnight. A similar effect has been noticed by Kenrick⁽⁹⁾. In figure 7 (January 26–27, 1933), which is typical of many records, the splitting of the echo between 1900 and 2300 indicates weakness of the ionization, and the rejoining of the split echo near 2300 indicates a reconcentration. The splitting and disappearance of the echoes just before sunrise corresponds to the ordinary decrease in ionization-density at this time. Records on a wave-length of 75 m. in the summer indicate the same effect, but the conclusions to be drawn from them

* We are much indebted to Mr R. H. D. Mayall for help with this calculation.

are not so certain because at a height of 200 km. the night is very short at this time of the year.

Rukop⁽¹⁰⁾ has drawn attention to a phenomenon which he calls the *Abendkonzentration*. He observes that, with sufficiently short wave-lengths, the *F* echo is doubled during the day, but after sunset the two components join together to give a single echo which later splits and finally ceases to be reflected in the usual manner. We, also, have observed this behaviour on several occasions throughout the year, whenever the wave-length used was nearly enough critical for the *F* region. By using the circularly polarized receiver we find that the upper echo during the day corresponds to the "ordinary" left-handed polarized wave; observations of the intensity confirm this, since this echo is always the stronger. It is possible that this daytime splitting is due to group retardation in the ledge which Appleton⁽⁴⁾ has shown to exist on the lower side of the *F* region, and that the disappearance of the splitting in the evening is due to the disappearance of this ledge by recombination. Appleton's figure 2 shows the same kind of midday splitting on a wave-length of 75 m. A similar phenomenon, often observable at the sunrise period, is illustrated in figure 8 (March 22, 1933) and can probably be explained in the same way. At 0630 the extraordinary echo appears and at 0850 the ordinary, which descends nearly to the level of the extraordinary at 0930 only to rise again immediately and stay at a considerably greater height than the ordinary until 1220, when the record finishes. This record, taken with a circularly polarized receiver, illustrates the nature of the polarization of the two echoes. If the present explanation is the correct one, there is no need to postulate the presence of an evening concentration of ionic density as suggested by Rukop.

§ 4. NOCTURNAL *E* IONIZATION

In the previous paper it was suggested that nocturnal increases of the ionization in region *e* might be due to charged solar corpuscles, such as are supposed to produce disturbances in the earth's magnetic field; or to the action of thunderclouds, as suggested by C. T. R. Wilson. We have now sufficient data to investigate whether there are any correlations between the nocturnal increases of ionization and magnetic disturbances or storm clouds. Appleton and Naismith⁽²⁾ have pointed out that they have very often found magnetic activity to be associated with an increased ionization "in the Kennelly-Heaviside layer," and other workers have occasionally noticed the same phenomenon⁽³⁾. A preliminary examination of our records shows, however, that there is by no means a one-to-one relation between the occurrence of nocturnal *e* ionization and either thunderstorms or magnetic disturbances, and that a statistical investigation is necessary before any relation can be established. Thus on the night (April 30–May 1, 1933) of commencement of the largest magnetic disturbance in the period under review, there was no record of nocturnal ionization in region *e*, even on a wave-length of 150 m. which was not far from being critical for the *E* region. On several occasions records on 75 m. wave-length showed absence of nocturnal region *e* ionization even when world-wide magnetic storms were recorded; since, however, 75 m. is far from being the

critical wave-length for the daytime region, these observations are not particularly significant. On the other hand, nocturnal-region-*e* ionization was often recorded, on both wave-lengths, when the night was magnetically quiet. In view of these results it seems essential to make a statistical analysis before any relation can be established.

In searching for a relation between the nocturnal ionization in region *e* and magnetic disturbances, we have distinguished between magnetically quiet and magnetically disturbed nights by taking the range of the variation of the magnetic declination through the hours of darkness and comparing it with the mean value of this range over the month in which the night occurred. Nights with a range greater than the monthly mean were classed as disturbed, and those with a range less than the mean as quiet. The magnetic data were taken from the figures published by the Abinger Magnetic Station, Surrey.

In the present experiments the wave-lengths used were 75, 150 and 200 m. It was found that the wave-lengths 150 and 200 m. nearly always showed some echo from region *e* or *E* during some part of the night; nocturnal-region-*e* ionization was only considered to be present if the ionization was sufficiently strong to prevent the signal from reaching the *F* region, or if the *e* echo was recorded during a period when at least one of the magneto-ionic components of the *F* echo was absent on account of electron-limitation. The nocturnal-*e* ionization was considered to be absent if the total duration of the *e* reflection, between the time when the daytime *E* echo disappeared in the evening and the time when it reappeared in the morning, was less than 15 minutes. This classification excludes several of the records on 150 and 200 m. which show simultaneous echoes from the *e* or *E* and *F* regions. On the wave-length 75 m. the borderline cases are much less numerous, and the classification into "nocturnal *e* present" and "nocturnal *e* absent" is simple. Table 1 summarizes the results which have been found. The numbers represent frequencies of occurrence, e.g. the number in the left-hand top corner is the

Table 1.

	Magnetically disturbed	Magnetically quiet
Nocturnal <i>e</i> present	39	55
Nocturnal <i>e</i> absent	19	63

$$\chi^2 = 6.7, p = 0.01.$$

number of nights which were disturbed and also showed nocturnal-*e* ionization. We find that of the disturbed nights 67 per cent show nocturnal-*e* ionization, whereas of the quiet nights only 46.5 per cent show it. This indicates that if the night is disturbed there is a greater tendency for nocturnal-*e* ionization to be recorded. The fact that so many quiet nights show nocturnal ionization is perhaps to be expected in view of the fact that the occurrence of the nocturnal-*e* echo merely indicates an increase of the ionization density in a somewhat localized region

immediately above the point of observation, whereas an increase of ionization would have to take place over a fairly large region before it could produce an appreciable effect on the earth's magnetic field. If, in spite of this, the results show a relation between the two phenomena, then we may conclude with some certainty that the magnetic disturbance is related to the nocturnal-*e* ionization.

In order to decide whether table 1 indicates any relation between the occurrence of nocturnal-*e* ionization and magnetic disturbances we use the statistical χ^2 test of independence*. The table gives a value of χ^2 equal to 6.7 corresponding to a probability of 0.01 that the same distribution should occur by chance if the two observed effects were completely independent. The conclusion to be drawn is that magnetic disturbances are very probably related to increases of ionization in the *e* region. Although the observations here described are concerned only with nocturnal increases of ionization, it is not suggested that daytime increases are absent.

Observations of the kind here described cannot be used to determine the cause of the ionization, but it is interesting to note that there is a marked tendency for the ionization to occur at nearly the same times on successive nights; this phenomenon would favour the theory of a corpuscular jet radiating from the sun.

It is next of interest to examine whether any relation is found between the occurrence of thunderstorms and of the nocturnal-*e* ionization, as might be expected from Wilson's(s) theory. The results of the year's observations are summarized in table 2, in which the occurrence of thunderstorms in the British Isles is compared with the occurrence of the nocturnal ionization.

Table 2.

	Thunder	No thunder
Nocturnal <i>e</i> present	34	60
Nocturnal <i>e</i> absent	12	70

$$\chi^2 = 10, p = 0.0015.$$

The table shows that 74 per cent of the thunderstorm days showed nocturnal-*e* ionization, whereas ionization occurred on only 46 per cent of the days with no thunder. Applying the χ^2 test we find a value of χ^2 equal to 10 and corresponding to a probability of 0.0015 that this distribution should occur by chance, if thunderstorms and the nocturnal ionization were unrelated.

The fact that the nocturnal-*e* region ionization is correlated with both thunderstorms and magnetic storms suggests immediately that the double correlation may be due to a direct relation between thunderstorms and magnetic storms. The data which have been used in drawing up tables 1 and 2 show no such relation; a similar table comparing the occurrence of thunderstorms with that of magnetic storms gives a value of χ^2 equal to 0.017 and corresponding to a probability of 0.9 that the observed distribution would occur by chance if the two phenomena were unrelated.

* See, for example, R. A. Fisher, *Statistical Methods for Research Workers* (Oliver and Boyd, 1930).

§ 5. ACKNOWLEDGMENTS

In August 1932 the recording apparatus was completely rebuilt, with a more powerful transmitter and a more robust receiving arrangement, with the assistance of the Department of Scientific and Industrial Research, who, on the advice of the Radio Research Board, have made a loan to us of the necessary apparatus. They have also provided us with cathode-ray oscillographs and photographic paper. We wish to take this opportunity of thanking them for their help.

We wish also to express our thanks to Prof. Appleton for many helpful discussions in connexion with the interpretation of the records; to Dr Wishart, of the Cambridge University Department of Agriculture, for help with the statistical analyses; to Prof. Stratton for continuing to provide us with an ideal site for our transmitter at the Solar Physics Observatory; and to Mr J. L. Pawsey for considerable help with the recording apparatus.

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DISCUSSION

Prof. A. O. RANKINE. May I seize this opportunity of getting from the lips of experts an explanation of what appears to be an inconsistency in relation to wireless transmission? It is very commonly believed that signal-strength is greater across the night side of the earth than the day side. Yet we have just learned, in this and the previous paper, that reflection from above is exceptional or feeble during the night, owing to insufficient ionization in the appropriate layer. If vertical echoes are stronger during the daytime, how is it that oblique ones are apparently weaker?

Mr A. E. BENNETT took exception to the use of the term "echoes." He suggested that the impulses received back from the ionosphere are re-radiations due to resonance.

AUTHORS' reply. Prof. Rankine's question is best answered by a reference to Mr F. W. G. White's paper. Mr White shows that the reflected wave may be unduly weak for two different reasons. Either it may be weak because there is not a sufficient electron-density in the reflecting region to return it to the earth—this is electron-limitation; or it may be weak because the electron-density in the absorbing regions of the ionosphere is so great that, although the wave is reflected, it is strongly absorbed—this is absorption-limitation. Thus, for vertical incidence, a wave may be weak during the day on account of absorption-limitation, and weak or absent at night owing to electron-limitation. For more oblique incidence, however, the electron-density required to produce reflection is not so great, and, for the long-distance transmission referred to by Prof. Rankine, electron-limitation does not usually occur, so that by night the signals are quite strong.

THE PRODUCTION OF SOUNDS FROM HEATED METALS BY CONTACT WITH ICE AND OTHER SUBSTANCES

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ABSTRACT. Experiments in which very loud notes were produced as a result of contact of metal bodies with solid carbon dioxide have been described in a previous communication*. The present paper is concerned with the conditions under which soft notes may be produced from heated metal bars brought into contact with ice and a number of other substances. These substances must either sublime or boil or decompose with the evolution of gas, at temperatures for which the metal to be excited still retains adequate vibrating properties. The experiments confirm the theory regarding the mechanism of the phenomenon which was developed in the previous paper. They establish the general conditions under which elastic vibrations of audible frequency may be excited in a metallic body, when contact with another cooler solid substance results in the production of gas from the latter.

§ 1. INTRODUCTION

THE conditions under which loud sustained notes may be produced by bringing metal bodies into contact with solid carbon dioxide have been fully described in a previous communication†. This phenomenon, as has already been mentioned in that paper, led to the discovery that small momentary notes may be produced from heated metals when brought into contact with ice, a fact which would otherwise almost certainly have remained unnoticed.

Some of the conclusions reached in the above communication will now be reviewed, and the observations which have been made on several heated metal bars—ice and a number of other materials being used to set them vibrating—will then be described.

(i) Solid carbon dioxide excites metal bars whose natural vibration frequencies may vary from about 1000 to 15000 ~. In preliminary experiments a few of these bars differing widely in frequency were heated, and it was found possible to set them into vibration by contact with ice. There is thus in the case of excitation by ice (or presumably by the other substances used) a wide range of audible frequencies which can be produced.

(ii) Various shaped bodies—bars, rings, tubes, bells, discs, etc.—can be set into vibration by contact with solid carbon dioxide. It has been considered sufficient to restrict the present study to metal bars, and to assume that bodies of other shapes could be excited if heated suitably.

* *Proc. Phys. Soc.* 45, 101 (1933).

† *Ibid.*

(iii) The phenomenon depends upon the transference of heat from metal to solid carbon dioxide. If metal bars are to be excited by ice, etc. they must be raised to a suitable temperature.

(iv) The body must possess adequate vibrating properties. In the case of excitation by ice or other suitable materials, the variation of this property with temperature has therefore had to be considered; see § 3 below.

(v) The mechanism of the excitation of vibrations, depending upon the sublimation of solid carbon dioxide with the production of considerable gas pressures when it is brought into light contact with the metal, would appear to be somewhat similar to the production of edge tones.



Figure 1. Schlieren photograph of carbon-dioxide sublimation caused by contact with edge of tuning fork.

(By courtesy of the Research Laboratory, General Electric Company, Ltd.)

Through the courtesy of the Research Laboratory of the General Electric Company, Ltd., the author has been able to study the effect on the quantity of gas produced of varying the degrees of contact between a metal bar or tuning fork and a block of solid carbon dioxide, by the Schlieren method, and a photograph very kindly taken by that Company is reproduced in figure 1. The photograph is of a fork viewed end-on, so that the shadows of the prongs are seen in cross section and merge into one. The solid block of carbon dioxide is touching an edge near the tip of one of the prongs, and two streams of carbon dioxide can be seen emerging in definite directions at right angles to the length of the fork. The block was pressing slightly on the edge, and the fork was chattering as well as vibrating regularly. When the contact is light and a pure loud note is being emitted, so little gas is

produced that the two gas streams are barely visible. This fact is of interest and is to be expected, for the contact is slight and intermittent, the condition is one of resonance, and since the damping of the fork is small little energy is required to maintain the vibration. The frequency of the fork being $3000 \sim$ and photographic exposure $\frac{1}{80}$ sec., sixty contacts take place during exposure, and individual puffs of gas cannot of course be observed.

The Schlieren method of observing the phenomenon thus confirms the theory of the production of the vibrations previously advanced, but shows how little sublimation occurs when loud pure notes are being produced. It would be of interest to observe the Schlieren image through stroboscopic apparatus in order to determine whether the puffs are on alternate sides as they are in the case of edge tones.

§ 2. EXPERIMENTAL ARRANGEMENTS

The bars used were 15 cm. long and of $\frac{1}{2}$ in. square cross-section. They were suspended from two nodes so as to vibrate transversely as free-free bars. The dimensions chosen are convenient for purposes of heating by means of either a blow-pipe flame or an electric oven. Such bars cool at a convenient rate, their vibrations persist for a suitable length of time, and lastly their frequency of vibration is in the region of greatest sensitivity of the ear, which is especially desirable as the notes produced are very soft.

Measurement of temperatures. In preliminary experiments the temperatures were roughly estimated by dropping the bars into a calorimeter containing a known mass of water. It was found for example with a brass bar, that the range of temperature over which notes can be produced by contact with ice was roughly from 100° to 200° C. The notes are accompanied by the hissing of the steam and are quickly quenched by water. At lower temperatures the metal eats its way silently into the ice block, producing water.

In some experiments in which the bars were heated in an electric oven the temperatures were measured by means of a mercury thermometer placed in the oven. It is to be noted that the loudness of the notes produced is not appreciably altered, although the surrounding air as well as the metal is now hot.

Another method for measuring temperatures, used in the case of a brass bar, was to solder a brass and constantan wire at the two nodes respectively, so that the wires fulfilled the double function of suspending the bar and enabling its temperature to be determined thermoelectrically by connecting the two wires with a shunted galvanometer. The wires were soldered into small holes bored into the upper surface of the bar, and interfered but slightly with its vibrating properties.

In most experiments two identical bars, one the vibrator and one the measurer of temperatures, were used. They touched along one edge while being heated, and were subsequently separated so that the former could be conveniently set vibrating. With a bar 15 cm. long it is easy to ensure that the temperature along it is practically uniform. In experiments with a bar, the temperature of which was measured at

the centre and one end by boring two holes and inserting two thermometers in them, the best routine for heating by means of a gas flame was established, and it was found that the temperature of the two thermometers tended to become sensibly equal fairly rapidly even if one was 5° or 10° C. above the other to begin with. The arrangement proved very satisfactory and experimental errors are generally much less than 10 per cent.

Detection of sounds produced. The sounds produced by means of any of the substances tested, other than solid carbon dioxide, are soft and of short duration. They can be heard in a quiet room, and the results given below were detected by ear alone. The author is indebted to Mr G. E. H. Rawlins for constructing a stand for holding the bar and a suitable arrangement for amplifying the sounds, for purposes of demonstration. A light microphone attached to the bar was eventually replaced by a more satisfactory arrangement of ear-phone coils and magnets which were fixed opposite a small piece of iron attached to a side of the bar near one of its ends. The coils were connected to amplifying valves and a loud-speaker.

By this means it would doubtless be possible to extend the list of compounds found to produce notes in heated bars, for the arrangement not only amplifies the note but also eliminates extraneous noises due to boiling, etc., which otherwise tend to mask it.

§ 3. VIBRATING PROPERTIES OF METALS AT DIFFERENT TEMPERATURES

A note on this subject follows the present paper*. The vibrating properties of metals usually decrease with temperature, and the upper limit of temperature for which it is possible to produce notes by contact of a metal bar with ice or other exciting substance is usually determined by this physical factor.

The results obtained for commercially pure copper, aluminium and zinc are shown in figure 2 and for medium steel in figure 3, where the vibrating properties, as determined by the duration in seconds of audibility of a note emitted by the vibrating bar, are plotted against the corresponding temperatures. The bars were struck with a hammer and the time for which the sound remained audible was noted by means of a stop-watch.

It will be noticed that the duration of audibility becomes too small to be measured by means of a stop-watch in the case of the particular samples of zinc, aluminium and copper at about 50° , 150° and 250° C. respectively.

Thereafter the melodiousness of the note decreases with rising temperature until at a higher temperature the pitch is no longer recognizable. It is to be noted that the frequency of the note varies but slightly at different temperatures, since the temperature variations of elasticity and density are both small. The vibrating properties of mild steel reach a minimum at about 120° C. and a maximum at about 240° C., after which there is a gradual decrease with rising temperature, the pitch however being still recognizable at a dull red heat.

* Page 124 of this volume.

§ 4. EXPERIMENTAL RESULTS

The metals used for establishing the conditions necessary for the production of notes in heated bars when brought into contact with various exciting materials were zinc, aluminium, copper, mild steel (or steel), and a number of the results

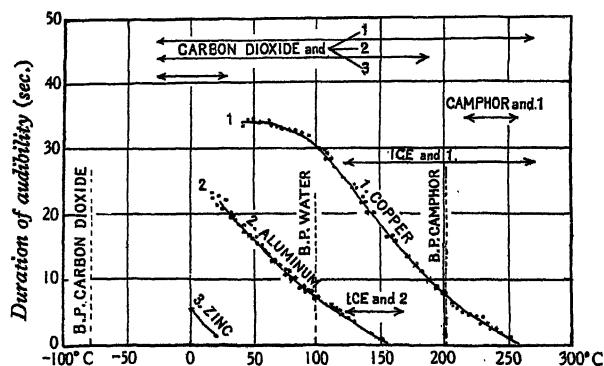


Figure 2. Vibrating properties (as measured by the duration of audibility of notes) of (1) copper, (2) aluminium, (3) zinc at different temperatures. The horizontal lines show the range of temperatures for which notes may be obtained from these metals when brought into contact with various exciting substances.

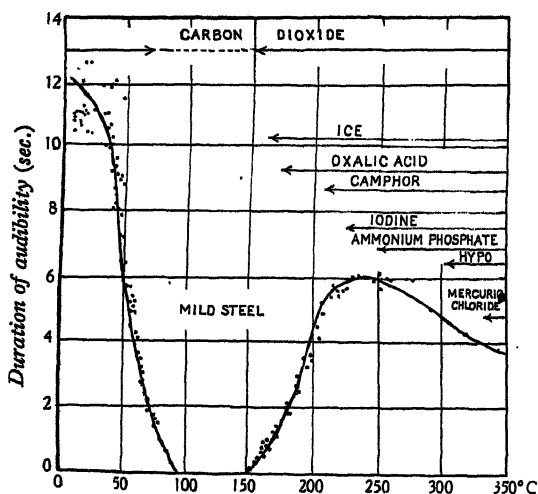


Figure 3. Excitation of notes from heated mild steel by contact with various exciting substances.

obtained are shown graphically in figures 2 and 3. The horizontal lines show the approximate range of bar-temperatures necessary for the production of notes with various pairs of metals and exciting substances. We proceed to consider some of the exciting materials used.

Ice. It is impossible to excite notes from zinc by means of ice, whereas carbon dioxide will produce loud notes. Aluminium, copper and most metals can however

be excited to give soft notes if they are heated above 120°C . and brought into contact with a block of ice. The lower limit of temperature, about 120°C ., does not differ very greatly from the temperature necessary to produce the spheroidal state, which is about 140°C .

As is shown graphically in figure 2, the upper limit of temperature is determined by the diminution in the vibrating properties of the metal and is about 150°C . for aluminium and 250°C . for copper. Reference to figure 3 shows that in the case of mild steel the lower limiting temperature, about 160° , depends upon the poor vibrating properties at that temperature and not on the boiling-point of water. The upper limit is not much below the temperature of red heat.

Contact between the ice and metal should be light. The note is somewhat masked by the hissing of the steam (unless it be listened to through the amplifier), but while it lasts it is pure and the phenomenon is similar to that of excitation by solid carbon dioxide, though on a very much smaller scale. The rapid formation of water soon quenches the soft sound.

Camphor, $\text{C}_{10}\text{H}_{16}\text{O}$, passes through a pasty condition in passing from the solid to the gaseous state, its melting-point being 170°C . and boiling-point 204°C . Care must be taken to prevent a flow of hot camphor over the fingers. As is shown in figure 2, notes cannot be produced in zinc or aluminium and only over a very limited range of temperatures, from about 220°C . to 260°C ., in copper. Mild steel will be excited between about 220°C . and a much higher temperature.

Iodine, the melting-point of which is 116°C . and boiling-point 184°C ., is harder to manipulate on account of the small size of the crystals. Notes have however been produced in mild steel above 230°C . (see figure 3) by holding the crystals by means of forceps.

We have seen that vibrations are produced in a metal bar on account of the gas pressure which results from the sublimation or boiling of the several exciting materials so far considered. It would seem probable, therefore, that materials which decompose with the evolution of gas when brought into contact with heated metals would also be capable of exciting vibrations in heated bars. Again, it might be possible to produce vibrations by means of crystals which give up their water of crystallization when brought into contact with the heated bar.

An exhaustive search on these lines has not been undertaken, but the results obtained with a number of crystalline compounds show that gas evolved as a result of chemical decomposition may produce soft notes over suitable ranges of temperature, whereas the vapour produced as a result of the liberation of water of crystallization is not sufficiently vigorous in its action to produce audible vibrations.

The experiments were generally made on a heated mild steel or steel bar, since these possess good vibrating properties at higher temperatures than the other metals used. The principal results obtained are summarized below and in some cases appear graphically in figure 3.

Oxalic acid, $\text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, produced notes when brought into contact with the bar heated to temperatures above about 175°C ., on account of sublimation and decomposition with the liberation of carbon-dioxide gas.

Mercuric chloride, HgCl_2 , produced notes when the bar-temperature exceeded 330°C . Mercuric chloride is generally said to sublime, its melting-point being 277°C . and boiling-point 304°C . Wet drops which evaporate rapidly form on the bar when this is touched on its upper surface.

Ammonium phosphate, $(\text{NH}_4)_2\text{HPO}_4$, produced notes when the bar-temperature exceeded 250°C . These are due to decomposition with the liberation of ammonia gas. A boiling deposit which forms on the bar damps the vibrations.

Sodium thiosulphate or "*hypo*," $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, produced notes, which are probably due to sulphur vapour, above 300°C .

Zinc nitrate, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, produced notes when the bar-temperature exceeded 150°C ., probably on account of nitrous fumes and oxygen.

Meta or metaldehyde, which sublimes between 112° and 115°C ., will produce notes in mild steel above about 240°C . The block has to be pressed against the heated metal and the note produced, though easily heard at higher temperatures, is not pure. In the case of meta we have passed a long way from the production of notes by solid carbon dioxide, in which (i) contact must be the lightest possible; (ii) the solid carbon dioxide offers a hard background; (iii) the sublimed carbon dioxide remains in the gaseous condition instead of immediately condensing into flakes; (iv) the notes produced are pure, loud and sustained.

Examples of substances which have failed to excite audible vibrations are: benzoic acid, potash alum, manganese sulphate, sodium sulphate, copper sulphate, borax, sodium carbonate, potassium nitrate, ammonium chloride, and ammonium carbonate. The results obtained will not be described in detail; each material behaves individually, and there may be hissing or silence, a deposit due to dehydration or decomposition which sticks on the bar, or a mass which gradually melts. Again if chemical decomposition occurs at a high temperature, for example in the case of potassium bromide, there is no effect, just as a material with an elevated boiling-point would produce no effect. Finally it is necessary that the crystals should be of a reasonable size: notes cannot be produced by means of powders.

§ 5. CONCLUSIONS

(i) Light contact made between two solid bodies which are at different temperatures may result in the production of elastic vibrations of audible frequency in the hotter body.

(ii) The hotter body must be a good thermal conductor, be capable of vibrating at suitable frequencies (about 1000 to 10,000 ~) and possess adequate vibrating properties at temperatures which exceed by some degrees the subliming, boiling or decomposing-temperature of the cooler exciting substance. Vibrations are not produced unless the metal is heated above these temperatures. The upper limit of temperature for which notes may be excited is determined by the loss of vibrating properties of the metal.

(iii) Apart from solid carbon dioxide, which would appear to be unique (at any rate among materials at present available) in its capacity to produce very loud notes,

there are a considerable number of materials which may be used to excite soft pure notes of short duration in heated bars. The mechanism of production is identical with, but on a very much smaller scale than, that of solid carbon dioxide.

Such materials are: (a) Those substances which sublime or boil at suitable temperatures when brought into contact with heated metals, for example ice, camphor, iodine, and mercuric chloride. If the sublimation is immediately followed by a return to the solid state in the atmosphere, as in the case of "meta," contact must be heavier and the note produced is not pure. Again the formation of liquid, as in the case of ice, soon quenches the note. (b) Substances which decompose when brought into contact with the heated metal with the production of gas pressure, as for example oxalic acid, ammonium phosphate, sodium thiosulphate and zinc nitrate. Solid deposit, or a melting or boiling mass on the metal, is a frequent cause of failure to produce notes with certain other compounds.

(iv) Notes have not been produced when certain compounds containing water of crystallization have been dehydrated by contact with the heated metal.

(v) If a more comprehensive study were contemplated of chemical compounds which will produce notes from heated metals it would be desirable (a) to amplify the notes and isolate them from extraneous noises due to boiling, etc., as described in the paper; and (b) to use a bar made of a metal which will vibrate at high temperatures, for example steel or monel metal or invar.

DISCUSSION

See p. 126.

NOTE ON THE VIBRATING PROPERTIES OF METALS AT DIFFERENT TEMPERATURES

BY MARY D. WALLER, B.Sc., F.INST.P.

Received July 1, 1933. Read November 3, 1933.

ABSTRACT. A simple acoustical method of studying the vibrating properties of metals at different temperatures is described. Since the damping of the vibrations, which is mainly due to internal friction or solid viscosity, is greatly altered either by previous heat or mechanical treatment and by impurities, i.e. is not constant at any given temperature, such a method capable of giving numerous comparative data over wide ranges of temperature should be of value. Furthermore, there is promise that on account of the large variations of the vibrating properties with temperature it will be possible to obtain, by observations of irregularities in these variations, much interesting information regarding the state of metals and alloys at different temperatures.

THE variation with temperature in the vibrating properties of several metals has been studied incidentally in the preceding paper* and a few results are there shown in figures 2 and 3.

The simple hand-and-ear method of observation by which these results have been obtained is now being used to carry out a survey of the vibrating properties of pure metals and alloys of known type between the temperatures of liquid air and red heat.

The author since developing the method has learnt that in 1911 F. Robin† used an essentially similar acoustical method for studying the vibrating properties of various metals between room temperature and red heat, and he was the first to draw attention to what he called the "aphonia" of carbon steels at about 120° C.‡. He used a standard impulse to set the bars vibrating, but the author finds that on account of the logarithmic nature of the damping, the magnitude of the impulse given to the bar may vary over wide limits without appreciably altering the duration of audibility of the note.

The method as used by the author consists in suspending a bar of square or circular cross-section, of side or diameter 0.5 in. and length 15 cm., from two nodes so that it may vibrate transversely as a free-free bar, heating it to known temperatures§, striking it a smart blow with a hammer held in the hand, and determining, by means of a stop-watch, the number of seconds for which the resulting note remains audible to the same observer listening near the bar with the same ear. Properly employed the method is satisfactory, and the degree of accuracy can be gauged by

* Page 116 of this volume.

† Iron and Steel Institute, *Carnegie Scholarship Memoirs*, 8, 125 (1911).

‡ See figure 3 of the preceding paper.

§ *Ibid.* § 2.

the lie of the experimental points on the curves. The irregularities may prove to be of significance, and not merely due to experimental errors. Losses of energy to the supports, provided these are suitably chosen, or on account of radiation of sound are of secondary importance, but as the research develops they may have to be considered. The most serious damping is due to formation of water drops below the dew-point, and to a lesser extent to the formation of hoar-frost in bars which are cooled to low temperatures in liquid oxygen. If comparisons between different bars are to be made, the frequency of the bar must be taken into account in order to determine the damping per cycle and to allow for varying sensitivity of the ear to different frequencies.

Again, no comparisons or specific constants of different metals can be given unless the exact composition, the degree and length of heating, annealing, cooling, etc., and the amount of working on the metal are known. Thus, for example, commercially pure copper bars purchased from two different dealers, and practically identical as regards dimensions, elasticity and density, vibrated for 3 and 20 seconds respectively at room temperature.

The field that may be investigated by the method would appear to be a wide one. The vibrating properties vary by very large amounts as the temperature changes, whereas many physical properties change but slightly with temperature. If relations can be established between the vibrating properties and certain physical conditions which are hard to detect, the method may be of practical use in the workshop. Properties which depend not only on the composition but on the treatment of the material, such as hardness, tensile strength, fatigue limit, etc., may bear some relation to the vibrating properties.

It is interesting to compare figure 3 of the author's paper cited above with Cuthbertson's* curve for the fatigue limit at different temperatures of medium carbon steel, which shows a very sharp minimum in the fatigue limit at 123° C. Again, the variation of the specific heat with temperature is such that a sharp maximum occurs at about 120° C. in the curve given by Dearden†. The curves given by Thompson and Whitehead‡ for the variations in specific resistance and thermoelectric power include maxima at this same temperature. Sauveur and Lee's§ figure 1 relating tensile strength and temperature of iron and steel shows a marked minimum at 100° C. for electrolytic iron. Herbert in the discussion on Cuthbertson's paper|| compares the working properties of iron at 120° C. to those of stiff putty or plasticine.

These considerations are sufficient to indicate that a study of the vibrating properties by the method indicated, simple and merely approximate though it may be, is worth while. Its chief virtue lies in the fact that very numerous observations may be made on a property which varies greatly when either the temperature, the composition or the treatment of the material is varied. Irregularities obtained in

* *J. Iron and Steel Inst.* 126, 237 (1932).

† *Iron and Steel Institute, Carnegie Scholarship Memoirs*, 17, 89 (1928).

‡ *Proc. R.S. A* 102, 587 (1923).

§ *J. Iron and Steel Inst.* 112, 324 (1925).

|| *Loc. cit.* p. 260.

curves promise to yield much interesting information in view of the present rapidly increasing knowledge of the metallic state.

It may also be possible to compare results with those given by more refined methods for the viscosity of various metals. These are limited in number and often contradictory, see for example the summary given by Erk*. The contradictions are not surprising once it is fully realized that whereas the viscosity of gases or liquids has a definite value for any given temperature, the viscosity of a metal can be enormously altered by mechanical and heat treatment, and by the addition of very small amounts of impurity. Ultimately no study of the damping forces or viscosity of metals will be complete without a knowledge of the crystalline condition of the particular specimen.

DISCUSSION

Prof. MARTIN KNUDSEN. I should like to point out the existence of the radiometer force which exists between two bodies in a gas when they are at different temperatures. Thus, suppose that we have two bodies at temperatures θ_1 and θ_2 in a gas at a pressure p , then the radiometer force exerted on every square centimetre of the opposite faces of each is equal to $\frac{1}{2}p\{\sqrt{(\theta_1/\theta_2)} - 1\}$, provided that their distance apart is negligible compared with the mean free path of the gas.

Suppose now that $\theta_1 = 800^\circ \text{ K.}$ and $\theta_2 = 200^\circ \text{ K.}$ The radiometer force is then equal to $\frac{1}{2}p$, so that if the pressure be atmospheric a force equal to half an atmosphere is exerted on every square centimetre of the opposite faces of each body, and thus if one body be fixed the other body will be forced away from it until the radiometer force becomes small, when, if there be a restoring force, the body will return to be forced away again by the radiometer force. Thus vibrations depending on the vibrational properties of the body will be set up.

If, as in the present case, gas be evolved, this will give an additional force which may be sufficient for the explanation of the vibrations. I wish only to emphasize that the radiometer force should also be taken into account in the explanation.

Mr C. R. DARLING. I should like to ask whether Miss Waller is of opinion that the vibrations are not in any way due to alternate contraction and expansion, as in the case of the Trevelyan rocker. Can invar, which is practically non-expansive, be made to vibrate by touching with a cold solid?

The extension of this work to the investigation of the properties of metals at different temperatures may prove of great service, as the experimental work is simpler than that involved in other methods having this object, and the results are equally certain.

Mr T. SMITH. I should like to call attention to a misleading word which enters into Miss Waller's paper by the merest chance. About twenty years ago one of my colleagues at the National Physical Laboratory had occasion in a paper to mention Töpler's Schlieren method. Shortly afterwards the late Lord Rayleigh referred to

* *Z. f. Metallkunde*, 6, 185 (1929).

this, and pointed out that the method should be known as Foucault's. Since that time I have endeavoured, though not with unvarying success, to persuade members of the N.P.L. staff who apply this method in various ways to adopt Lord Rayleigh's advice. It would help towards a correct understanding of the history of physics, which is so difficult nowadays for students to acquire, if we avoided using terms which tend to mislead, of which many examples besides "schlieren" might be mentioned. I suggest that the Physical Society should, as opportunities occur, call attention to widespread errors of this kind, and endeavour to bring about their general correction.

AUTHOR'S reply. I should like to thank Prof. Knudsen for his interesting remarks regarding the magnitude of the radiometer pressure and its possible contribution to the production of vibrations. It is not, however, possible to get any sign of vibration when a heated metal is touched with another cold body which does not emit gas. The mean free path of air being only about 10^{-5} cm. at atmospheric pressure, and the contact being necessarily light and between two small areas, one of which is irregular, it would appear that the radiometer force must be very small.

Mr Darling raises an important point. I have repeated the experiments, and do find that it is easier to produce notes in iron than in invar, though the pure sustained notes are about equal in loudness. The two materials are comparable as regards thermal conductivity, elasticity, density and vibrating properties, and having regard to experiments made on other metals I am inclined to think that a large coefficient of expansion is a contributory though not a principal cause of the production of vibrations.

With regard to Mr T. Smith's remarks I agree that scrupulous care should be taken to see that honour is given where it is due. A. Toepler introduced the term *Schlierenapparat** to describe the apparatus which was used to detect the *Schlieren* or streaks in imperfect glass. He has added footnotes in both publications, from which we learn that Kirchhoff drew his attention to Foucault's work on the examination of optical surfaces published in the *Annales de l'Observatoire Impérial de Paris*, 5, 203. He recognizes that his and Foucault's methods are very similar in principle. The word *Schlieren* does not occur in most German dictionaries; its meaning is given as "streaks (in glass and igneous rocks)" in Patterson's *German-English Dictionary for Chemists*. Since therefore the word is not an ordinary one and the method promises to be used commercially, and since Foucault and Toepler's work was independent and devised for different purposes, it would seem better to speak of the Foucault-Toepler method.

* *Ann. d. Phys.* 128, 126 (1860); 131, 35 (1867).

ADDENDA TO DISCUSSIONS

Discussion of paper entitled "The influence of atmospheric suspensoids upon the earth's electric field," by H. L. WRIGHT, M.A., *Proc. Phys. Soc.* **45**, 152 (1933).

The AUTHOR. The following footnote appears on p. 154: "According to an investigation carried out by Prof. Whytlaw-Gray, on behalf of the Atmospheric Pollution Research Committee of the Department of Scientific and Industrial Research, the number of particles given by the Owens instrument is about a fifth of the number present in the air and large enough to be seen by a microscope. The details of this investigation have not yet been published." This statement, which refers to a comparison of the jet dust-counter with a method of counting, developed in the course of Prof. Whytlaw-Gray's investigation, in which the particles are deposited by thermal action, was inserted as having an obvious bearing on the subject-matter of my paper. I am informed, however, that the result which was quoted was both premature and incorrect. Subsequent work has indicated that the two methods give counts of the same order. It is regretted that the quotation of the result of what, as I now learn, was in fact an incomplete investigation should have given currency to a misleading statement concerning the performance of the jet dust-counter.

Discussion of paper entitled "A note on the Kerr cell," by E. E. WRIGHT, B.Sc., *Proc. Phys. Soc.* **45**, 469 (1933).

Dr A. NARATH. In dealing with the distortions obtained in modulating the characteristic of a Kerr cell, the author appears to have been unaware of certain earlier papers dealing with the same subject. For instance F. Fischer and H. Lichte* have ascertained the distortions of a Kerr cell in terms of Fourier components by the use of Bessel functions. This deduction is identical with that of E. E. Wright. In a different way the present writer in the same year calculated the non-linear distortions in a Kerr cell, tested the deduced relations by experiments, and verified them†. The above papers go further than the paper under discussion, since in addition to the percentage of harmonic waves the rectifying action is calculated and the deduced relations have undergone a thorough experimental test and verification.

AUTHOR'S reply. The method of effecting the Fourier analysis adopted by Fischer and Lichte differs somewhat from that employed by me, and none of the Fourier amplitudes are given explicitly. Further, the analysis is used only to deter-

* *Tonfilm, Aufnahme und Wiedergabe nach dem Klangfilm-Verfahren*, pp. 236-238. (Hirzel, Leipzig, 1931.)

† Lecture at the Deutscher Physikertag, Bad Elster, in 1931; *Z. f. technische Physik*, **13**, 17 (1932).

mine the distortion for the two bias values, $V/2$ and $V/\sqrt{2}$, and not for determining the position of minimum distortion. Apart from these differences, however, I have to admit that this reference is very pertinent to my own work. On the other hand, I would like to point out that the book is not readily available in England; for example, there is no copy in the Library of the British Museum. Dr Narath's own paper is very extensive and interesting but I consider that it is less relevant as an anticipation of my analysis, since the expressions obtained in it for the amplitudes of the components are in the form of doubly infinite series and are, I think, less suited to computation than mine, in spite of the fact that the use of Bessel functions is avoided.

REVIEWS OF BOOKS

A Text-book of Physics. Volume 2, Heat and Sound, by E. GRIMSEHL. Edited by R. TOMASCHEK. Authorized translation from the 7th German edition by L. A. WOODWARD. Pp. xii + 312 with 225 figures, numerical tables and examples. (London: Blackie and Son, Ltd.) 12s. 6d. net.

This is the second of a comprehensive series of text-books of physics of which the first three have now appeared. References are given in Volume 3 (Electricity) to articles in Volume 5 which has not yet been published.

The present volume could be read with interest by apprentice engineers, but the same criticism applies that has been made with regard to Volumes 1 and 3: the presentation is not sufficiently formal for serious students of physics. For them many of the otherwise excellent figures will be wasted, as for example that of the Babcock and Wilcox boiler with superheater on p. 157, and the force-transmission to the crank of a six-cylindred motor, p. 171, which is incomprehensible. This engineering aspect is marked in table IV b, p. 291, which gives the temperatures at which the vapour pressure of water is 1, 2, 3, etc. kg./cm².

The subject-matter of heat goes as far as elementary considerations of entropy, but the fact that the simple Carnot cycle is nowhere represented in ϕ , θ coordinates, that the fundamental researches of Rowland and of Reynolds and Moorby and their significance in the philosophy of the subject are absent, and also that the work of Callendar and Barnes is relegated to an appendix, will be sufficient to indicate that the publishers' claim that the standard is that of a degree in physics is scarcely justified.

There are some excellent figures and diagrams in the chapters on wave motion and sound. The structure of the text calls for little comment. The physical presentation is better here, but there is a marked absence of any references to the mass of very interesting modern researches.

The index needs revision. There is no reference to the singing flame (p. 296) or to viscosity (p. 291).

L. S.

A Text-book of Physics. Volume 3, Electricity and Magnetism, by E. GRIMSEHL. Edited by R. TOMASCHEK. Authorized translation from the 7th German edition by L. A. WOODWARD. Pp. xiv + 660 + pp. 10 of numerical examples. (London: Blackie and Son, Ltd.) 25s. net.

This book, like the volume on mechanics by the same author, should appeal to a much wider circle than those working for "a degree in physics," to quote from the publishers' advertisement. One can browse amongst the pages, each of which has its interesting pictures or diagrams, and some pages have three or four diagrams. These range from a full-page catalogue reproduction of a modern screening couch and X-ray apparatus down to a picture of a tumler switch.

The volt-ampère system of units is used throughout. As the author says in the preface, every physicist employs only instruments calibrated according to this system and has an intuitive appreciation of the significance of the quantities employed. Thus we see on p. 178 the statement "The unit of magnetic field strength H is that field strength which exists in a long solenoid through which is passing a current of one ampère per cm. length." I cannot gather the meaning of this. The system of units throughout the book has this

basis. The only parallel case that has come into common usage in physics recently is the nomenclature for the velocity of an electron in terms of electron-volts, but I doubt if the accepted usefulness of this term would be taken to be a justification for altering the whole fabric of systematic physics.

In spite of the fact that this book presents a very interesting appearance, the careful students of physics reading it will be on nodding but not familiar terms with principles. In the long run it will be far better to jettison all the repetitive detail that does not help to advance the subject.

L. S.

The Development of Physical Thought, by L. B. LOEB and A. S. ADAMS. Pp. 648. (London: Chapman and Hall.) 23s.

A welcome may be given to this general survey of physics, which formed the basis of lectures given to a class "open to all letters and science students regardless of class and irrespective of previous exposure to high school physics." The book is not exhaustive, but is divided into six chapters, of which the first is historical, giving an account of some of the principal movements of scientific thought from early times to the foundation of the Royal Society and after.

On p. 50 is a graph which is supposed to give the number of significant discoveries as a function of time in years. Whether this curve has much validity is to be doubted, but it does illustrate the enormous growth of research towards 1900. It is then asked if this acceleration of output is to continue, and the conclusion is suggested that knowledge will increase at an almost constant rate.

It is questionable whether "in Oxford even now, a scientific worker or student is looked upon with scorn by the classicists."

Chapter 2 is devoted to mechanics. Admirable features, in contrast to the general development of the subject, are the detailed treatments of the inclined plane and lever to which many measurements, systematically arranged, are appended.

On pp. 157 and 445 an account is given of the Michelson-Morley and kindred experiments, such that the reader is left with the impression that no ether wind has been detected. Later work by Miller, Courvoisier, etc. would indicate that the question is perhaps not finally settled. On p. 165 it is stated that "it was not until 1919 that President Campbell of the University of California and members of his expedition were able to make a successful and accurate set of observations of the positions of the stars in the neighbourhood of the sun during an eclipse." Some reference to the work of Dyson, Eddington and Davidson seems to be called for.

Chapters 3 and 4 deal with heat and classical electricity respectively. Chapter 5 is given to light, which is rather briefly treated in some thirty pages. The spectroscope, for example, has a very scant description. Chapter 6 gives a very full and interesting account of modern electrical work on the structure of matter and allied topics. Many photographs illustrating the work of C. T. R. Wilson, Blackett, Feather and others are reproduced from the pages of the *Proceedings of the Royal Society*. Considerable attention is devoted to the atomic discoveries of the last few years, and it would be a dull student indeed, who could not find an interest in this last almost romantic chapter.

The book contains over one hundred figures, those of apparatus being simplified to the last degree.

Finally there is a bibliography of literature suitable for further reading, a table of physical constants and nearly thirty pages of index.

To supplement work with a more conventional text-book, this volume giving side-lights on physics as a development of thought will be extremely attractive to any student with an enquiring mind.

J. E. C.

Analytic and Vector Mechanics, by HIRAM W. EDWARDS, Ph.D. Pp. x + 428. (McGraw-Hill Book Company, Inc., 1933.) 24s. net.

This book gives a general account of the principles and methods of dynamics up to a standard which is rather higher than that of the general B.Sc. degree in the University of London, but not quite sufficient for the Special Honours degree. There are many points in the book to be greatly welcomed. The introduction of brief historical references does a great deal to add a certain human interest to a subject which can be rather arid and abstract, and the quotation from Newton on p. 128 will come as a surprise and an inspiration to many students.

Again, the introduction of vectorial methods is extremely useful in abbreviating some of the demonstrations, particularly in obtaining the fundamental equations of uniplanar rigid kinetics. It seems to the reviewer, however, that the use of vectors does very little to simplify the theory of the general motion of a rigid body as exemplified in tops and gyroscopes; and that the deduction of Kepler's first law by vectorial methods given on pp. 262 and 263 is unnecessarily clumsy. The method employed in the book makes use of the concept of the reciprocal of a vector, but this concept is nowhere defined, nor are the properties of the reciprocal of a vector investigated in any other part of the book. This is particularly unfortunate in view of the fact that the method employed in these pages is only successful because the vector denoted by A^{-1} is perpendicular to the vector r .

The equations of motion are treated on the basis of Newton's laws made palatable by the method used by Appell. No critical account of the foundation of the subject is attempted, and the reader will be bitterly disappointed with the paragraph headed "Standard Reference System" on p. 2.

D'Alembert's principle is not explicitly mentioned until the last chapter, although it is of course used in obtaining the equations of motion of a rotating body in chapter 8. In fact the proof of D'Alembert's principle is left as an exercise for the student!

The greater part of this work is taken up with dynamics, but there are also included one chapter each on statics, attractions and potential, and vector fields. The reader accustomed to the treatises of Loney and Lamb will be disappointed at the small number of exercises included in the book. However, he will also be pleased to note a few original examples, e.g. the deflection of an alpha particle by a movable nucleus, the sky rocket, the water stream and bucket.

Personally I feel that this book falls between two stools. There is not sufficient analysis for the mathematician and there is not sufficient experimental illustration for the physicist. Finally, I have very serious doubts whether the introduction of vectors at this stage does effect any real simplification. In spite of all these criticisms, it must of course be recognized that the author had a very difficult task before him. None of the existing text-books on this subject is completely satisfactory, and Prof. Edwards has made a most courageous attempt to provide a more acceptable text-book on mechanics. G. T.

Practical Acoustics for the Constructor, by C. W. GLOVER. Pp. xi + 468. (London: Chapman and Hall.) 25s. net.

The past few years have seen published a spate of books upon the subject of architectural acoustics; their outlook, their treatment, their length and their style have varied considerably but among them the present volume must be regarded as unique. In character it is essentially a book of applied science and contains those minutiae of detail and that wealth of illustration which are associated with a volume devoted to engineering design.

In his preface the author professes the aim of providing a vade mecum for the practical man and, bearing this in mind, we must condone the absence of formal proofs, which the purist might regard as a sin of omission, and also consider leniently sins of commission in the nature of diagrams popular rather than scientific in their appeal. It must not, how-

ever, be imagined that the book belongs to the "Wonders of Science for the Man in the Street" series, as Mr Glover is equally at ease in constructing the exercises appended to each chapter, and in summarizing in a most valuable manner the Bureau of Standards sound insulation values for various partitions, as he is in indicating the method of concealing nail heads when fixing board absorbents.

Adhering to convention, the opening chapters are devoted to a general discussion on the subject of sound. While we note a measure of confusion between intensity and loudness, and some numerical inexactitude associated with the description of stationary waves, we heartily commend, as a device appreciated by students, the use of a diagram of the genealogical-table variety which sets out the scope of the subject in a clear and instructive manner. Broadly speaking the matter reported in the body of the book is that common to other treatises on the same subject, except that we do not remember having encountered elsewhere chapters devoted to the organ and its position in an auditorium, or to aircraft noise: we also consider that the photographic illustrations and drawings of constructional details are more prolific than usual.

Not the least remarkable features of the volume are the chapter on acoustical specification clauses and the series of appendices, which, to the practitioner, must be worth almost the cost of the book. The first appendix is a somewhat haphazard list of books and papers concerned with acoustics, vibration and noise; the second a summary of acoustical defects together with their remedies; the third a list of no fewer than seven hundred and two absorbent materials together with their absorption coefficients over considerable frequency ranges; and the last, illustrated particulars of over forty acoustical materials. Our only possible grievance is that the author, for fear of controversy and invidious comparison, was deterred from inserting cost data in appendix 3, but nevertheless we must conclude by expressing to Mr Glover our appreciation of his generosity in divulging so many mysteries of his craft in such a painstaking and interesting manner. E. J. I.

Gyroscopic Stabilisation of Land Vehicles, by J. F. S. Ross, B.Sc., Ph.D. Pp. vii + 172. (London: Edward Arnold and Co.) 14s. net.

This book discusses in the first 100 pages the mathematical requirements for the stability of such vehicles. From the equations of motion the usual periodic equation, a linear differential equation of the fourth order, is derived. The conditions that this equation shall represent two damped oscillations are then discussed at unnecessary length*. Numerical examples are given and suggestions for a design to incorporate the essential controls for stability are added.

The rest of the book is devoted to a criticism of the designs of the pioneers in this field of work, Brennan, Scherl, Schilovsky and others. No description of the apparatus used is given, but the patent descriptions are discussed in the light of the essential requirements shown by the analysis of the periodic equation. The author evidently does not like discontinuous control. Brennan's ingenious reversal of the friction couple by means of his dead and live rollers and Schilovsky's spasmodic engagement of the precessional torque are disapproved.

If ever the monorail is adopted in practice, the method of controlling the gyroscopic precession may be continuous or discontinuous, but the reasons retarding its adoption are not due to any failure to understand the scientific requirements. The parallel problem of the damping of the rolling of ships is an engineering success.

The book will appeal mostly to students of a mathematical bent who will find many interesting problems in it. An excellent glossary is given at the end.

* This equation occurs in many gyroscopic problems and is dealt with very shortly in a paper by Prof. Sir J. B. Henderson in the *Proceedings of the International Mathematical Congress at Toronto*, 1924.

Elements of Engineering Acoustics, by L. E. C. HUGHES. Pp. xi + 159. (London: Ernest Benn, Ltd.) 8s. 6d. net.

The scope of this book is indicated by its seven chapter-headings, which are: Sounds and Sound Systems, Sound-Field and Sound Measurements, Reproduction of Sound, Electro-Acoustic Measurements, Microphones, Amplifiers, and Reproducers; and its substance has already been published by the author in a series of articles in the Students' Section of the *Electrician*. On account of this origin a somewhat disjointed text might be anticipated, but in actual fact Dr Hughes, in his rôle of editor, has given us a general if slightly dogmatic discussion of his subject in the form of a continuous narrative, which, regarding perspicuity of text as the hall mark of a good book, we should have preferred to find more frequently broken by paragraph headings.

We commend in particular the final chapters dealing with the microphone-amplifier-reproducer system, and note with interest what the author has to say on the subject of *acoustic distortion*.

While we may perhaps be permitted to deprecate mildly the inclusion of a picture of (mainly) four valves bearing the legend "Loaded Push-Pull Power Amplifier," and the designation of ultrasonic waves of high intensity as a "form of death ray", our repudiation must take a stronger form when we learn that to obtain different frequencies we merely require suitable taps on an a.-c. mains transformer. On the other hand we receive with personal satisfaction Dr Hughes's somewhat unorthodox contention that musical experts or musicians are of no use in assessing the quality of reproduction of music save when it is very bad.

If we may appear hypercritical it is because we welcome a book covering the field treated by an author who speaks with authority and whose message we would, for others as well as ourselves, desire to be as easily assimilable as possible. E. J. I.

Recent Advances in Physical Chemistry, by S. GLASSTONE, Ph.D., D.Sc., F.I.C. Pp. viii + 498. (Second Edition. London: J. and A. Churchill.) 15s.

The fact that a new edition of Dr Glasstone's excellent summary of some of the more notable advances in physical chemistry should be called for within two years of the publication of the first edition is sufficiently convincing testimony of its value. The author has taken the opportunity to include in the new edition a large mass of fresh material, and has discussed briefly the application of wave mechanics to problems of valency and to the calculation of the energy of activation; nuclear disintegration, the neutron and the positive electron; the influence of free and restricted rotation on dipole moments; molecular beams; potential-energy curves; atomic reactions; the kinetics of photochemical reactions; activated and discontinuous adsorption; surface potentials; and the mobility of surface molecules. A very useful chapter on solubility has disappeared, but even so the present edition is longer by some thirty pages than its predecessor. Physicists who desire to know something of the central problems of modern physical chemistry and of the outlook of the physical chemist of to-day will find Dr Glasstone's book of great service. A. F.

An Introduction to Thermodynamics for Chemists, by D. JOHNSTON MARTIN. Pp. vii + 343. (London: Edward Arnold and Co.) 16s. net.

We may not all agree that it is a good thing to write books on thermodynamics for engineers, for chemists, for horticulturists... but it is certain that the chemist has a compelling interest in many topics that are best treated with the assistance of a thermodynamical argument. A book, therefore, which gives a perfectly sound and general discussion of the bases of modern thermodynamics, and afterwards proceeds to apply these

principles to physico-chemical topics, has ample *raison d'être*. The author's introductory chapters are scholarly, and he is thoroughly alive to the presence of those pitfalls which lurk ready to entrap the unwary and facile reasoner. In the part of his text which deals with applications he has treated very fully dilute solutions, the activity method of treatment of solutions, the theories of strong electrolytes, chemical affinity, and heterogeneous systems.

Following the work of Lewis and Randall, the author has discussed very fully the distinction between free energy and maximum work. He has produced a very serviceable volume, which should find wide acceptance.

A. F.

Introduction to Physical Chemistry, by ALEXANDER FINDLAY. Pp. vii + 492. (London: Longmans, Green and Co., Ltd.) 7s. 6d.

Prof. Findlay is not afraid to begin at the beginning, and has given us, in rather less than five hundred pages, a text-book which is a model of what such a book should be. Starting with the very elements of the subject, he develops a course which holds the balance admirably between the old and the new, between theory and experiment, and leaves the student with nothing to unlearn when he proceeds to more specialized study. The topics of a course of degree standard are treated of succinctly and thoroughly, very full references to original sources are scattered through the text, and an appendix furnishes a number of numerical examples which may serve to test the reader's knowledge. The book may be unreservedly recommended. It is well produced and illustrated and is, at the price, remarkably good value.

A. F.

Correction Tables for Use with Platinum Resistance Thermometers, by G. S. CALLENDAR and F. E. HOARE. (London: Edward Arnold and Co.) 1s.

These tables have been computed so that the labour of reducing readings with a platinum resistance thermometer is reduced to a minimum. Nowadays when a platinum resistance thermometer is selected for the measurement of moderately high temperatures, the reason is that by means of it temperature-measurements of high precision can be made. On this account it is desirable to have tables for the conversion of platinum temperatures to the international scale worked out to a high order of accuracy, and in the present tables the corrections are given to several places of decimals. The main table covers the range 0 to 1000° C. In addition a table is given of the corrections to be applied when in the well-known difference formula the delta is not exactly 1.5.

To anyone concerned with resistance thermometry the table will prove a sound investment.

E. G.

Photograms of the Year 1933, edited by F. MORTIMER, Hon. F.R.P.S. Pp. 24 with 64 plates. (London: Iliffe and Sons, Ltd.)

"This here science, it keeps going on," and it is odd to think, in an age of cinematographic cameras capable of taking records at the rate of thousands a second, that in the youth of our parents a visit to the photographer held almost as many terrors as a twentieth-century visit to the dentist. The maiden of the 'fifties or the 'sixties, swathed in voluminous and unsightly garments, and clamped, as to the back of her head, in a steel contraption designed to hold her steady during an exposure, has left us photographic records of herself which are studies not so much of a human being, as of a "head sticking out of a dress."

That is an accusation which certainly cannot be laid against many of the delightful personal studies—sometimes graceful, sometimes bizarre—in the volume under review. Seascape and landscape; the human model; still life studies, orthodox and unorthodox;

the suggestion of immense force latent in a crank-shaft and locomotive driving-wheel, and of skill and artistry in a hand engaged in fine lace manufacture—nothing comes amiss to the modern camera artist. To the lore of the man with the palette he has added a technique peculiarly his own, which is abundantly exemplified in the reproductions given in this most interesting and valuable record of the progress of camera art in 1933. A. F.

Liquid Crystals and Anisotropic Melts. A General Discussion held by the Faraday Society. Pp. iv + 204. (London: Gurney and Jackson, 1933.) 12s. 6d. net.

The present volume, reprinted from the *Transactions of the Faraday Society*, contains twenty-four papers and a general discussion. The continental authors include Vorländer, Kast, Ornstein, Ostwald, Rinne and Zocher, and the English authors Bernal, W. H. Bragg, Crowfoot, Fowler, Lawrence and Malkin. Ornstein and Zocher discuss rival theories of liquid crystals, Rinne emphasizes their biological importance, Lawrence deals with lyotropic mesomorphs and Bernal and Crowfoot contribute a study of the true crystalline phases of substances which form liquid crystals. In their paper, Bernal and Fowler deal with the structure of ice. The accepted structure has been modified, the unit cell being much larger and the structure molecular; four molecules are arranged in approximately tetrahedral fashion around a fifth. This arrangement in conjunction with Prins's theory is used to explain the X-ray diffraction patterns of water and their change with temperature. Water changes from something approximately ice-like at low temperatures to a quartz-like structure at ordinary temperatures, and further heating tends to produce close packing. The whole volume will be of considerable interest to those concerned with structural physics and chemistry, particularly from the point of view of the transition from the solid to the liquid state. J. R. P.

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NOTE ON THE BEHAVIOUR OF THE EÖTVÖS GRAVITY BALANCE IN FLUCTUATING GRAVI- TATIONAL FIELDS

By PROF. A. O. RANKINE, O.B.E., D.Sc., F.INST.P.

Received November 28, 1933. Read December 15, 1933.

ABSTRACT. In this note attention is directed to the semi-diurnal variation of gravity at a point on the earth's surface, due to lunar attraction and recently measured by Loomis. It is shown that this temporal variation of g is much larger than the spatial differences measured by the Eötvös gravity balance, but that it produces no effect on the balance. This constitutes an experimental proof of the power of the Eötvös instrument to discriminate between space and time changes of terrestrial gravitation.

IN my presidential address to the Society* I remarked that the Eötvös torsion balance had so far been denied the opportunity of demonstrating its chief virtue, namely, its capacity for differentiating between temporal and spatial variations of the earth's gravitational field, by responding to the latter and not to the former. This remark was made without due consideration of the facts, and it is not true. I had forgotten that it has recently been established experimentally that there is a semi-diurnal fluctuation of g due to the gravitational attraction of the moon. Such variations have been implied, of course, ever since the origin of the tides was recognized, and G. H. Darwin calculated the effect more than fifty years ago. But it was not until 1931, when Loomis published† the results of his comparisons of Shortt clocks with quartz oscillators, and E. W. Brown and D. Brouwer‡ analysed these records, that the effect of the moon upon the period of a pendulum, and consequently upon g , was definitely measured. The results are of such significance in relation to practice with the Eötvös balance, and prove for it such a tacit triumph in its power of discrimination, that they deserve to be quoted in some detail.

The results of Loomis's comparisons show that the error of the Shortt clock,

* *Proc. Phys. Soc.* 48, 1 (1934).

† *M.N.R.A.S.* 91, 569 (1931).

‡ *M.N.R.A.S.* 91, 575 (1931).

as compared with the quartz oscillator which is independent of gravity, is given by the expression $-0.00015 \sin 2\phi$ sec., where ϕ is the difference between the longitude of the moon and that of the experimental station (at Tuxedo Park). The error is thus approximately semi-diurnal and of amplitude 0.00015 sec. Taking into account the dependence of the pendulum-period upon gravity we find that the corresponding small variation Δg of g is given by

$$\Delta g/g = -4.3 \times 10^{-8} \cos 2\phi,$$

which indicates a fluctuation of Δg of half-lunar-day period and ranging from $-4.3 \times 10^{-8} g$ when the moon is in the local meridian (or 180° from it) to $+4.3 \times 10^{-8} g$ when the moon is rising or setting. These values are for the latitude of Tuxedo (41° N.) and agree with the general formula derived from G. H. Darwin's theoretical investigation, namely

$$\Delta g/g = -7.7 \times 10^{-8} \cos^2 \lambda \cos 2\phi,$$

where λ is the latitude. At the equator the effect will be a maximum, and there the total change of g during the six lunar hours above mentioned will be $2 \times 7.7 \times 10^{-8} g = 1.5 \times 10^{-7} g$ approximately. Temporal fluctuations of this order of magnitude have certainly been occurring regularly ever since Eötvös initiated field practice with his balance, yet there is no record of their having produced any noticeable effect, even though a complete set of observations at a station often itself occupied six hours.

It is interesting to compare the relative magnitudes of the spatial variations which the balance has measured and the temporal variations to which it has remained irresponsive. We may take the time variation of g for the average latitude as, say, $10^{-7} g$, or 10^{-4} cm. sec.⁻². Compared with the magnetic diurnal variation this is relatively small*, but it bears a large ratio to the spatial differences actuating the Eötvös instrument. A good instrument of this type is sensitive enough to indicate a gravity-gradient of 1 Eötvös unit, or 10^{-9} sec.⁻², and its full scale seldom corresponds to more than a few hundred Eötvös units, say, 5×10^{-7} sec.⁻². The balance, in effect, measures the variation of g over a horizontal distance equal to the difference of level of the masses constituting its beam, and this is of the order 50 cm. Thus it will just indicate a change of g amounting to 5×10^{-8} cm. sec.⁻², and give full-scale deflection for 2.5×10^{-5} cm. sec.⁻². The temporal variation, attributable to lunar action, bears to these the ratios 2×10^3 and 4 respectively. It appears then that the Eötvös torsion balance has continued calmly and faithfully to record spatial variations of gravity only, while subjected also to temporal changes two thousand times as large as the least effect it could show, and four times the equivalent of its maximum recording-capacity. Surely a convincing practical proof of the virtue of the balance in discriminating between effects in space and time.

The explanation, of course, lies in the fact of the close approximation to spatial uniformity of the lunar gravitational field over the space occupied by the instrument, combined with its small value relative to the terrestrial field. We may thus confidently anticipate that the magnetic analogue of the gravity torsion

* The diurnal variation of H in London, for example, is of the order $2 \times 10^{-8} H$.

balance would be similarly immune from the effects of large-scale temporal changes of the terrestrial magnetic field, such as the diurnal fluctuations. It is true that the experimental proof of immunity does not extend precisely by implication to magnetic storms, for gravitational storms are rare events if we exclude the inappreciable effects of meteors. But there are no grounds for doubting that most magnetic storms, being of a widespread character, would also be ineffective in disturbing a magnetic torsion balance based on the same principles as the Eötvös gravity instrument.

DISCUSSION

Dr H. SHAW. It is interesting to note, in support of Prof. Rankine's paper, that when on occasions we have observed the torsion balance at hourly intervals continuously on the same station for several weeks, no temporal changes corresponding to the diurnal variations referred to, have been indicated by this instrument. The reason, as is explained in the paper, is that the lunar effect, which is of a temporal nature, gives rise to a practically uniform raising or lowering of the force of gravity over a large area, so that the values of the gravity-gradient and the differential curvature, which are measured by the torsion balance, are comparatively unaffected. In the case of very small and local disturbances, however, these give rise to a local deformation of the gravity surface which will be detected and measured by the torsion balance. Similarly it is reasonable to suppose that a magnetic instrument, such as the one referred to by Prof. Rankine, would not respond to extensive magnetic storms, but would be sensitive to small local disturbances, and so may be expected to be most useful in distinguishing between these two types of disturbances.

ON THE TEMPERATURE VARIATION OF THE ORTHOBARIC DENSITY OF UNASSOCIATED LIQUIDS

By ALLAN FERGUSON, M.A., D.Sc., F.INST.P., AND
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ABSTRACT. A formula connecting the orthobaric density of a liquid and its temperature is developed in the form

$$\rho = 2\rho_c [A(1-m)^{0.3} + (1-\frac{1}{2}m)],$$

where m is reduced temperature and A is a constant which varies slightly from liquid to liquid, and may be taken to have a mean value 0.91. The formula is a long-range one, and has been tested for thirty pure organic substances. It has been applied to the evaluation of expansion coefficients, and to show the manner in which free and total molecular surface energies vary with temperature.

§ 1. DEVELOPMENT OF THE FORMULA

SOME time ago, in a discussion on a paper by Dr Griffiths and Mr Awbery*, it was pointed out by one of us that a simple long-range formula could easily be established which should represent with very high accuracy the relation between orthobaric density and temperature for an unassociated liquid. In this paper we have worked out the constants of the equation for the thirty pure liquids whose pressure-volume-temperature relations have been studied by Prof. S. Young, and discussed in a paper which has become classic†. It is hardly necessary here to stress the importance of obtaining figures giving the thermal properties of liquids and vapours with a high degree of precision, or of developing equations which shall accurately represent these results. The present paper is a contribution towards the end last named.

Some years ago Macleod‡ proposed the equation

$$\gamma = C(\rho_l - \rho_v)^4 \quad \dots\dots(1),$$

connecting surface tension at any temperature with the corresponding values of the orthobaric densities of the liquid and its vapour. It has also been shown by one of us (A. F.) that the constant C may be expressed§ in terms of the critical constants. If we combine this equation with the power law|| connecting surface tension and temperature

$$\gamma = A(1-m)^n \quad \dots\dots(2),$$

* *Proc. Phys. Soc.* 44, 121 (1932).

† *Proc. R. Dub. Soc.* 12, 374 (1910).

‡ *Trans. Farad. Soc.* 19, 38 (1923).

§ *Trans. Farad. Soc.* 19, 17 (1923).

|| Van der Waals, *Z. f. Phys. Chem.* 13, 716 (1894); A. Ferguson, *Phil. Mag.* 31, 37 (1916).

where m is the reduced absolute temperature, and n a number which varies slightly from liquid to liquid, but which may be taken as equal to 1.2, we easily obtain

$$\rho_l - \rho_v = 4\rho_c (1 - m)^{0.3} \quad \dots\dots(3).$$

The constant of the equation is evaluated as $4\rho_c$ from the consideration that, when m is zero, ρ_v may be neglected, and ρ_l , the liquid density, may be taken as about four times the critical density.

The law of rectilinear diameters gives us

$$\rho_l + \rho_v = a - bm = 4\rho_c - 2\rho_c m \quad \dots\dots(4),$$

from the consideration just mentioned, together with the fact that when $m = 1$, $\rho_l = \rho_v = \rho_c$.

Hence, adding, we find

$$\rho_l = 2\rho_c [(1 - m)^{0.3} + (1 - 0.5 m)] \quad \dots\dots(5).$$

It is noteworthy that, if we may assume the constancy of the indices in Macleod's law and the power law, we have here a general relation between reduced density and reduced temperature which contains no constants depending on the properties of any one liquid. A similar equation may be obtained, of course, for the density of the saturated vapour.

Restricting ourselves to a consideration of the liquid density, and therefore dropping the subscript l , we may write equation (5) as

$$\rho/2\rho_c - (1 - 0.5 m) = (1 - m)^s \quad \dots\dots(6),$$

$$\text{or} \quad \log [\rho/2\rho_c - (1 - 0.5 m)] = s \log (1 - m) \quad \dots\dots(7),$$

where, for generality, we put s for the constant 0.3. A logarithmic plot should therefore give us a straight line through the origin, whose slope will determine s . The thirty pure substances mentioned, for which Young gives experimental values of ρ and m over their whole range of existence, have been tested in this way. Very satisfactory linear plots are obtained, but in no case does the line pass through the origin. If therefore we put

$$\rho/2\rho_c - (1 - 0.5 m) = X, \quad (1 - m) = Y \quad \dots\dots(8),$$

our line becomes

$$\log Y = s \log X + \log A \quad \dots\dots(9),$$

where A is determined from the intercept, and our final equation connecting ρ and m is

$$\rho = 2\rho_c [A (1 - m)^s + (1 - 0.5 m)] \quad \dots\dots(10).$$

In table 1 we show a conspectus of the results, giving the values of A and of s . It is noteworthy that the only serious deviations from the value 0.3 for the index s are those shown by the alcohols—typical associated liquids. A varies very little from liquid to liquid, and a reasonably satisfactory general formula for the temperature variation of the density of any unassociated liquid is

$$\rho = 2\rho_c [0.91 (1 - m)^{0.3} + (1 - 0.5 m)] \quad \dots\dots(11),$$

where mean values of A and of s are employed. If high accuracy is desired, account must be taken of the variation of A and of s from liquid to liquid.

Table 1. Values of A and s

Substance	A	s	Substance	A	s
Benzene	0.8790	0.3003	Normal hexane	0.8966	0.2938
Fluorobenzene	0.8831	0.2986	Normal heptane	0.9268	0.3000
Chlorobenzene	0.8995	0.3000	Normal octane	0.9473	0.2934
Bromobenzene	0.9033	0.2934	Isopentane	0.8728	0.3035
Iodobenzene	0.9103	0.3023	Di-isobutyl	0.9020	0.2837
Methyl formate	0.9192	0.3000	Di-isopropyl	0.8510	0.2798
Ethyl formate	0.9294	0.3035	Hexamethylene	0.8586	0.2957
Propyl formate	0.9389	0.3063	Acetic acid	0.9109	0.2914
Ethyl acetate	0.9512	0.3119	Carbon tetrachloride	0.8668	0.3000
Propyl acetate	0.9750	0.3113	Stannic chloride	0.9242	0.3146
Methyl acetate	0.9428	0.3050	Ethyl ether	0.9036	0.2944
Methyl propionate	0.9517	0.3094	Methyl alcohol	0.8855	0.2120
Ethyl propionate	0.9815	0.3161	Ethyl alcohol	0.8915	0.2068
Methyl butyrate	0.9583	0.3076	Propyl alcohol	0.8772	0.2048
Methyl isobutyrate	0.9482	0.3063			
Normal pentane	0.8764	0.2902	Mean values	0.9113	0.3001

* Excluded from mean value.

Obviously, the common assumption that $v_c = 4b$, where b is the constant of characteristic equations of the type

$$(p + \omega)(v - b) = R\theta,$$

—an assumption which we used in developing equation (10)—is not close enough. If we put m equal to 0 in equation (11) we find that

$$\rho = 2\rho_c (1.91) \text{ or } v_c = 3.82 b.$$

If we use equation (10) with the values of A and s appropriate to the particular liquid, the agreement with the experimental values is remarkably close. Table 2 shows the agreement between observed and calculated values for one of the sub-

Table 2. Methyl propionate

Temperature (° C.)	ρ observed	ρ calcu- lated	Temperature (° C.)	ρ observed	ρ calcu- lated
0	0.9387	0.9393	200	0.6445	0.6448
20	0.9151	0.9158	220	0.5938	0.5952
40	0.8912	0.8912	230	0.5635	0.5662
60	0.8665	0.8666	240	0.5220	0.5302
80	0.8408	0.8408	245	0.4976	0.5057
100	0.8137	0.8137	250	0.4665	0.4753
120	0.7852	0.7852	253	0.4401	0.4573
140	0.7553	0.7544	256	0.3982	0.4061
160	0.7221	0.7216	257.4	0.3124	0.3124
180	0.6856	0.6858	(Critical)		

stances—methyl propionate—selected at random. Figures 1 and 2 show respectively the straight line from which the constants are deduced and the march of the calculated and the observed values for fluorobenzene. It will be seen that, save for a limited region just below the critical temperature, observed and calculated

values agree within the limits of experimental error. At the critical point itself, the formula is adjusted to give exact agreement, and moreover dp/dm is, as it should be, infinite.

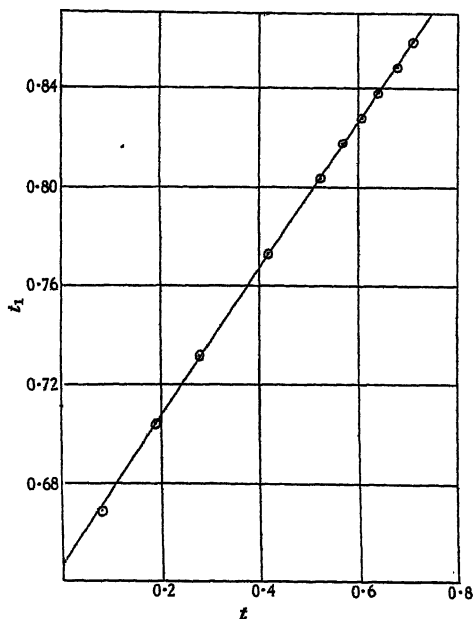


Figure 1. Fluorobenzene.

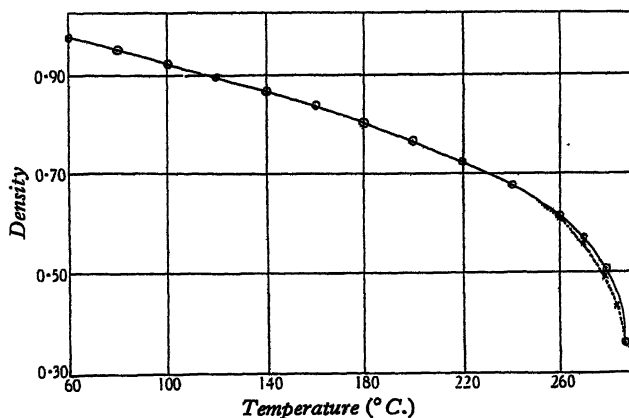


Figure 2. Fluorobenzene.

§ 2. APPLICATIONS

A long-range formula which possesses any pretension to accuracy will usually subsume a number of formulae of restricted application and should, indeed, indicate the reasons for the shortness of the range over which such formulae are valid. Equations (10) and (11) provide some interesting illustrations in the field of heat and of capillarity, one or two of which we proceed to discuss.

(i) Thorpe and Rucker suggested a number of years ago* that the critical temperature of an unassociated liquid might be determined from two observations of the density of the liquid, made at two not very widely separated temperatures (usually 0°C . and the boiling point). The formula proposed was

$$\theta_c = \frac{\theta_2 \rho_1 - \theta_1 \rho_2}{B(\rho_1 - \rho_2)} \quad \dots\dots(12),$$

where B is a constant whose mean value was taken as 1.99. The value of B was calculated for twenty-four substances for which the required data are known, and the extreme range of variation of B was from 1.93 to 2.03. Obviously, therefore, the formula cannot be expected to give very exact results. The boiling point of a normal liquid may be taken, very approximately, as 0.65 times its critical temperature, so that, employing reduced temperatures, and writing equation (12) as

$$B = 1.99 = \frac{m_2 \rho_1 - m_1 \rho_2}{\rho_1 - \rho_2} \quad \dots\dots(13),$$

we may put $m_2 = 0.65$, and $m_1 = 0.65 - \delta$, where δ is fairly small. If we now, using equation (11), calculate $(m_2 \rho_1 - m_1 \rho_2)$ and $(\rho_1 - \rho_2)$, we find that their ratio is independent of δ provided that we can neglect squares and higher powers of δ in comparison with unity. If the two temperatures chosen are close enough to make this assumption permissible, the value of the ratio is 1.9.

(ii) Thatt† has proposed an equation for the coefficient of expansion of a van der-Waals fluid in the form

$$\alpha = \frac{1}{v} \frac{\partial v}{\partial \theta} = \frac{1}{2.5 \theta_c - 2\theta} \quad \dots\dots(14).$$

We may write

$$\alpha = -\frac{1}{\rho} \frac{\partial \rho}{\partial \theta} = -\frac{1}{\rho \theta_c} \frac{\partial \rho}{\partial m} \quad \dots\dots(15),$$

in terms of reduced temperatures. The differential coefficient $\partial \rho / \partial m$ refers to orthobaric conditions, whilst that in equation (14) is taken at constant pressure, but the distinction is unimportant for the small values of m to which the argument is confined. If, taking equation (10) as basis, we evaluate the right-hand side of (15), writing it in the reciprocal form of (14), we find that, approximately,

$$\alpha = -\frac{1}{\rho \theta_c} \frac{\partial \rho}{\partial m} = 1 / \left\{ \frac{A+1}{As + \frac{1}{2}} \theta_c - \frac{A+1}{As + \frac{1}{2}} \left(\frac{As + \frac{1}{2}}{A+1} + \frac{As(1-s)}{As + \frac{1}{2}} \right) \theta \right\}.$$

If, as a first approximation, we put $A = 1$, $s = 0.3$ we find that

$$\alpha = 1 / (2.5 \theta_c - 1.66 \theta) \quad \dots\dots(16).$$

The closer approximation involved in giving A its mean value 0.91, leads to

$$\alpha = \frac{1}{2.47 \theta_c - 1.61 \theta} \quad \dots\dots(17).$$

The agreement with Thatt's formula is as close as can be expected, and the simple analysis shows clearly enough the conditions under which formulae of the type (12) or (14) hold good. Apart from the physical fact that the constant A does vary slightly from liquid to liquid—a fact which in itself sets a limit to the accuracy

* *Trans. Chem. Soc.* 45, 135 (1884); S. Young, *Stoichiometry*, p. 171.

† *Phil. Mag.* 7, 887 (1929).

of all such formulae—it will be apparent that the simplicity of the equations depends on the possibility of an expansion in which either the reduced temperature, or the difference of two reduced temperatures, is small.

(iii) Reverting to Thorpe and Rucker's problem of the calculation of a critical temperature from a knowledge of the density of a liquid at two temperatures which are well below the critical value, it is evident that the possibility of applying a simple formula is contingent on the temperatures being fairly close together. This suggests the use of a knowledge of the coefficient of expansion and of equation (17) to calculate an approximate value of the critical temperature. Failing this, Thorpe and Rucker's formula would give better results if the two temperatures at which the densities are measured were less widely separated.

(iv) It is desirable to be able to calculate an approximate value of the critical density of a fluid whose critical temperature is known. This is possible, to the limit of accuracy imposed by the variation of A in equation (10), from a knowledge of one value of the density, if we use the mean value of A given in equation (11). If, for simplicity, we choose a definite convenient value for m , say $m = 0.6$, and determine the density of the liquid at the corresponding centigrade temperature, we have, putting $m = 0.6$ in equation (11),

$$\rho_c = 0.3592\rho \quad \dots\dots(18).$$

The accuracy with which the critical density may be calculated from this simple formula is shown in table 3 below.

Table 3

Substance	Temperature (°C.)	ρ_t	ρ_c calculated	ρ_c observed
Benzene	63.7	0.832	0.298	0.304
Iodobenzene	159.6	1.620	0.581	0.581
Bromobenzene	129.0	1.345	0.483	0.485
Chlorobenzene	106.3	1.012	0.364	0.365
Fluorobenzene	62.7	0.971	0.349	0.354
Pentane	9.1	0.637	0.229	0.232
Hexane	31.6	0.649	0.233	0.232
Heptane	50.1	0.657	0.236	0.234
Octane	68.5	0.662	0.238	0.233
Isopentane	3.4	0.626	0.224	0.234
Hexamethylene	58.8	0.741	0.266	0.273
Di-isobutyl	56.8	0.662	0.237	0.236
Di-isopropyl	27.1	0.655	0.235	0.241
Ethyl acetate	40.8	0.875	0.314	0.308
Propyl acetate	56.5	0.848	0.304	0.296
Methyl acetate	33.4	0.916	0.329	0.325
Ethyl propionate	53.5	0.852	0.306	0.296
Methyl propionate	45.2	0.885	0.318	0.312
Methyl butyrate	59.5	0.854	0.307	0.300
Methyl isobutyrate	51.3	0.853	0.306	0.301
Acetic acid	83.7	0.979	0.352	0.351
Stannic chloride	82.0	2.066	0.742	0.742
Ethyl formate	31.9	0.907	0.326	0.323
Methyl formate	19.2	0.976	0.350	0.349
Propyl formate	49.6	0.870	0.313	0.309
Ethyl ether	7.0	0.728	0.262	0.262
Carbon tetrachloride	60.6	1.515	0.544	0.558

(v) The formula may be used to establish the manner of the temperature variation of certain capillary constants of importance in physical chemistry. *Free* molecular surface energy e and *total* molecular surface energy E are defined by the equations

$$e = \gamma (M/\rho)^{\frac{2}{3}} \quad \text{and} \quad E = \lambda (M/\rho)^{\frac{2}{3}} \quad \dots\dots(19)$$

respectively, where M is the molecular weight of the liquid, γ its surface tension (or free surface energy), and λ its total surface energy. λ and γ are connected by the well-known relation

$$\gamma = \lambda + \theta \partial\gamma/\partial\theta \quad \dots\dots(20).$$

If we assume the power law (2) connecting surface tension and temperature, the equation which gives the variation of λ with temperature is, as was pointed out by Porter*,

$$\lambda = A (1 - m)^{n-1} [1 + (n - 1) m] \quad \dots\dots(21),$$

where we may put $n = 1.2$.

Combining these equations with the equation representing the march of density with temperature, which for convenience we shall put in its simplest form

$$\rho = 2\rho_0 [(1 - m)^{0.3} + (1 - \frac{1}{2}m)],$$

we easily find that

$$e = K \frac{(1 - m)^{1.2}}{[(1 - m)^{0.3} + (1 - \frac{1}{2}m)]^{\frac{2}{3}}} \quad \dots\dots(22),$$

and

$$E = \frac{K_1 (1 - m)^{0.2} (1 + 0.2 m)}{[(1 - m)^{0.3} + (1 - 0.5 m)]^{\frac{2}{3}}} \quad \dots\dots(23),$$

where K and K_1 are constants which may readily be evaluated in terms of the molecular weight and the critical constants.

The most direct way of exhibiting the variation of e and E with temperature is to work out the values of the multipliers of K and K_1 for different values of m and to exhibit the results graphically. It is common to assume that E is independent of temperature, and Bennett and Mitchell† have calculated values of E for a large number of substances, and obtained results which are deemed to support this conclusion. If we put

$$E = K_1 F, \text{ where } F = (1 - m)^{0.3} (1 + 0.2 m) / [(1 - m)^{0.3} + (1 - 0.5 m)]^{\frac{2}{3}},$$

we find, on calculating F for different values of m , the results given in table 4.

Table 4

m	0.0	0.3	0.5	0.6	0.7	0.8	0.9	0.99	1.00
F	0.630	0.680	0.711	0.724	0.735	0.738	0.720	0.575	0.000

Figure 3 shows the variation in F , and therefore the variation of the total molecular surface energy E with temperature. It will be seen that there is a slight but definite maximum at about $m = 0.79$.

* *Trans. Farad. Soc.* 17, 1 (1922).

† *Z. f. Phys. Chem.* 84, 475 (1913).

Now take Bennett and Mitchell's figures for, say, chlorobenzene. The critical temperature of chlorobenzene is 633° , the figures are given in table 5 and cover the range $m = 0.67$ to $m = 0.85$.

Table 5. Chlorobenzene

θ	423	433	443	453	463	473	483	493
E	1461	1462	1467	1469	1472	1470	1474	1471

θ	513	523	533	543	553	563
E	1468	1467	1467	1468	1461	1455

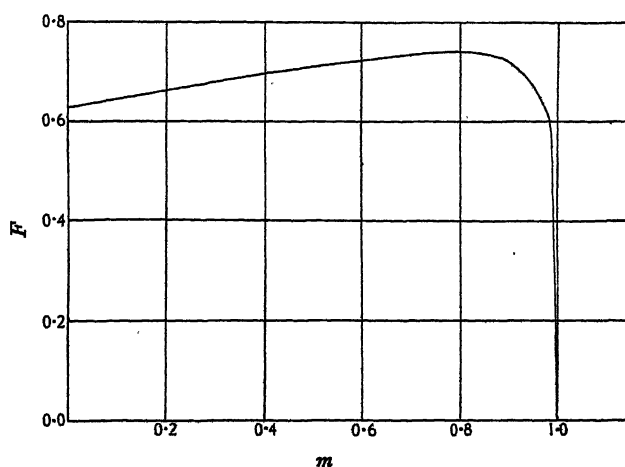


Figure 3.

These figures are usually quoted in support of the constancy of E , and the slight maximum which they show has in consequence been overlooked. Nevertheless the maximum is there, and occurs at about 483° , for which $m = 0.76$. This is in close agreement with the maximum given by the theoretical curve.

If we plot in similar fashion the multiplier of K in the expression for e , the resulting curve is indistinguishable from a straight line, except in a limited region near to the critical point. This is in accordance with the experimental results obtained by Ramsay and Shields.

We propose, in a future communication, to discuss the temperature variation of orthobaric vapour density, and the relation of saturated vapour pressure to temperature.

CRYSTAL STRUCTURE AND ORIENTATION
IN ZINC-OXIDE FILMSBY G. I. FINCH AND A. G. QUARRELL, Imperial College of
Science and Technology*Received October 27, 1933. Read December 15, 1933, with demonstration.*

ABSTRACT. A new type of electron-diffraction camera is described incorporating means for greatly increasing the accuracy hitherto obtainable in electron-diffraction analysis. Partially and completely oxidized zinc films have been examined by transmission. It has been found that the normal type of zinc oxide is formed by the oxidation of zinc via a zinc oxide which is basally pseudomorphic with the zinc. The corrosion-resisting properties of zinc appear to be due, in the main, to a protective coating of such pseudomorphic zinc oxide.

§ 1. INTRODUCTION

THE well-known phenomenon of pseudomorphism in crystal growth extends to all three dimensions. It has recently been shown, however, that when formed under suitable conditions thin films of aluminium on platinum, of zinc oxide on zinc, and of magnesium oxide on magnesium, possess abnormal crystal structures due to pseudomorphism confined to two dimensions*. For example, aluminium, normally of face-centred cubic structure ($a = 4.05 \text{ \AA.}$), when deposited as a sufficiently thin layer on normal face-centred cubic platinum ($a = 3.91 \text{ \AA.}$) acquired a face-centred tetragonal structure with basal axis 3.90 \AA. and major axis 4.02 \AA. Thus, within the then limits of experimental error, the aluminium was in its basal dimensions pseudomorphic with the platinum substrate. A similar effect was observed in the case of a thin film of zinc oxide on zinc (triangular close-packed lattice, hexagonal system; $a = 2.65 \text{ \AA.}$, $c = 1.95$). In this case, whilst the basal dimensions of the zinc oxide were similar to those of the zinc substrate, the major axis had increased from 5.18 \AA. , the value for the normal form of zinc oxide, to 6.79 \AA. Hence the volume of the cell of abnormal zinc oxide basally pseudomorphic with normal zinc was nearly equal to that of the normal zinc-oxide cell. The new phenomenon thus brought to light may conveniently be termed basal-plane pseudomorphism.

In the case of aluminium exhibiting basal-plane pseudomorphism with normal face-centred cubic platinum, it so happened that, owing to the doubling or trebling of certain rings, the diffraction patterns obtained were such as to establish clearly the face-centred tetragonal structure of such aluminium. On the other hand, with zinc oxide formed on zinc the type of crystal structure was found to remain unchanged. The accuracy attainable in the determination of lattice dimensions by

* *Proc. R.S. A* 141, 398 (1933).

existing methods of electron diffraction, however, proved to be amply sufficient for the purpose of establishing the occurrence of basal-plane pseudomorphism in this case also. Nevertheless, it was evident that in order to carry out effectively a critical search for a structure intermediate between one exhibiting full basal-plane pseudomorphism and the normal structure, it would be necessary to evolve means whereby the accuracy of electron-diffraction measurements might be greatly increased.

The accuracy of the determination of crystal-lattice constants by electron diffraction has hitherto been limited by various sources of error, chief of which is that due to the lack of precision attendant upon the measurement of high voltages. In addition, in the case of diffraction of an unfocused beam of electrons at grazing incidence, an uncertainty as to the effective camera length is introduced by the fact that the beam is divergent and the rings are correspondingly blurred. In what follows an account is given of an electron-diffraction camera which incorporates devices enabling these and other sources of error to be eliminated to such a degree that the accuracy attainable is comparable with that of the most precise X-ray methods of crystal analysis. With this camera a detailed examination of the structure of zinc—zinc-oxide films has been carried out, and the great gain in accuracy achieved has led, *inter alia*, to a new view of the causes affecting the distribution of the intensities of the rings in electron-diffraction patterns.

§ 2. EXPERIMENTAL

Owing to the sources of error outlined above, and notwithstanding many claims to the contrary, an accuracy greater than ± 2 per cent, when medium-speed electrons (above, say, 20 kV.) are employed for the determinations of lattice constants, can hardly be obtained with the methods hitherto in general use. It occurred to us, however, that it should be possible to eliminate such sources of error (i) by suitable electromagnetic focusing and biasing of the beam, and (ii) by comparison of the diffraction pattern of the substance under examination with that produced by a standard structure, the constants of which had been previously determined with the utmost accuracy possible with X-rays. In preliminary experiments the two patterns were superimposed by interrupting the exposure and bringing the reference material into the electron beam by suitable manipulation of the specimen carrier, and then completing the exposure. It was found, however, that the identification of the rings was frequently difficult and in many cases rendered uncertain owing to the coincidence of rings common to both patterns. Increased scattering due to the double exposure also added materially to the difficulties of measurement. Accordingly it was decided to attack the problem on lines analogous to those followed in spectrography. The principle finally adopted consisted in exposing one half of the photographic plate to the diffracted rays emanating from the one specimen and then exposing the other half to electrons diffracted by the reference specimen, the electron-beam axis, concentration and velocity remaining unchanged.

§ 3. THE CAMERA

The electron-diffraction camera was constructed by the Cambridge Instrument Company Ltd., and is shown in section in figure 1. Although essentially similar in design to a smaller camera described elsewhere*, it incorporated, in addition to a new type of shutter, certain other features which added greatly to the convenience and speed of operation and which will now be described.

Cathode chamber assembly. The glass vessel *A* was made from a straight-necked wine bottle. After the base had been cut off, the neck and body apertures were ground normal to the axis with carborundum paste on a copper block. The vessel was then sealed with picein wax into a groove in the brass block *B*, the lower surface of which was ground flat to make a vacuum-tight joint with the similarly ground and suitably lubricated upper surface of the anode block. The flanges *C* and *D* protected the picein and grease from bombardment by the discharge and consequent gas evolution. The cathode assembly consisted of a highly polished massive aluminium rod *E* screwed into the brass block *F*, the lower surface of which, covered by a thin greased rubber washer, formed a vacuum-tight joint with the neck of the bottle. Since this joint was easily made and broken it was a simple matter to withdraw the cathode for repolishing and to remove sputtered metal from the walls of the discharge vessel. It was thus possible, without inconvenience, always to operate the discharge under the most favourable conditions. In the event of damage to the glass vessel, replacement with retention of symmetry about the axis was a simple matter, because the type of bottle used was moulded.

Electron-beam trap. Owing to the intensity of the electron beam obtained by focusing, the exposure times required were never greater than $\frac{1}{2}$ sec., and difficulty was sometimes experienced in giving a sufficiently short exposure by hand operation of the shutter. An electron-beam trap was therefore incorporated in the instrument, enabling the exposures to be made and timed electrically. The trap, figure 1, consisted essentially of a trapping chamber *G* with a wide diaphragm situated in the axis of the main tube. By applying suitable potentials to the trapping plates *P*₁ and *P*₂, the electron beam could be caused to pass through the diaphragm or could be collected in the trapping chamber. In the case of reflection experiments the polarity of the trapping plates with the beam trapped was such that the beam was withdrawn behind the specimen.

Focusing-coil assembly. A bank of four coils, as shown in figure 1, electrically connected as two independent pairs, was adjustable into any position between the diffraction chamber and the main evacuation port. The axis of the coil could be inclined to that of the camera by means of the levelling screws *S*, enabling the electron-beam axis to be biased into any desired direction.

Specimen-carrier assembly. In the case of reflection experiments the specimen under examination was clamped side by side with the reference specimen on the plate *P*, provided with levelling screws by means of which the surfaces of the two specimens could be adjusted into a common plane perpendicular to the axis of

* *Loc. cit.*

rotation of the stem. The plate could be unscrewed from the stem and replaced by a similar plate or by a holder suitable for transmission experiments. Controls, the nature of which will be evident from figure 1, enabled the specimen to be adjusted as follows: (i) inclined to the electron beam, (ii) translated into the beam, (iii) rotated in the azimuthal plane and, finally, (iv) moved laterally in the specimen plane in a direction at right-angles to the beam.

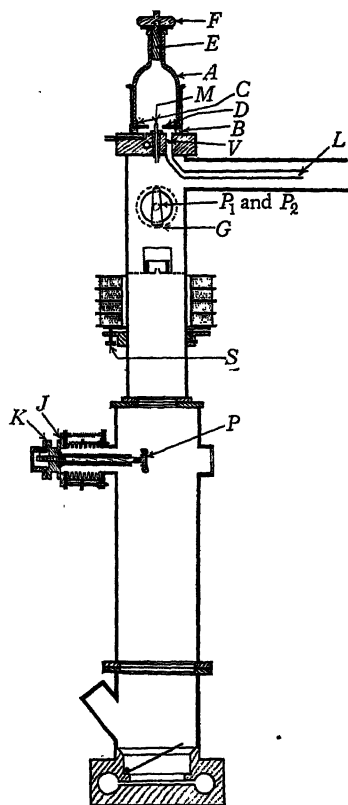


Figure 1. The electron-diffraction camera.

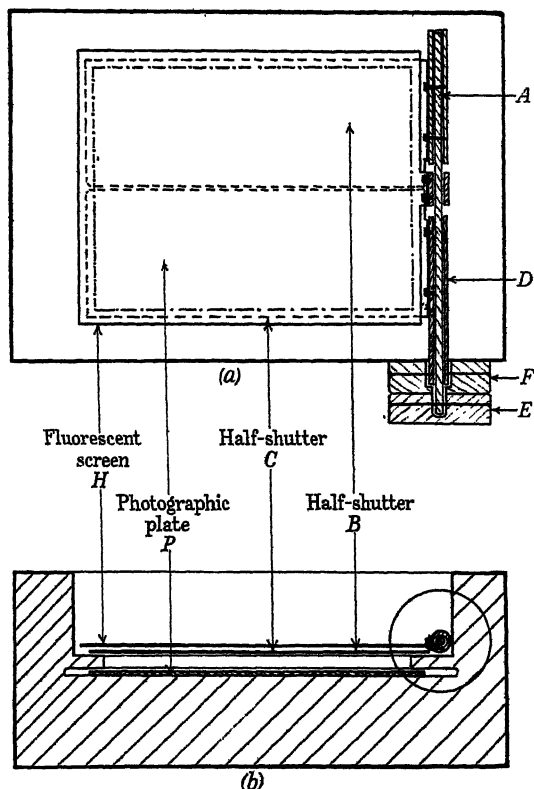


Figure 2. Details of camera shutter.

The necessary flexibility combined with vacuum-tightness in the assembly was obtained by means of two lapped surfaces at *J* and *K* and a short length of flexible metallic bellows*.

Camera shutter. The construction is shown in cross-section and elevation in figures 2 (a) and 2 (b) respectively. The fluorescent screen *H* was hinged to rotate freely about the stem *A*, to which the half-shutter *B* was secured. The other half-shutter *C* was similarly screwed to the tube *D*, concentric with *A*. Rotation through 90° of either head *E* or *F* raised the half-shutter *B* or *C* respectively, together with the loosely hinged fluorescent screen, thus exposing the corresponding half of the

* Replacement of the specimen-carrier section by a tube section fitted with crossed deflecting-plate pairs converted the instrument into a high-speed cathode-ray oscillograph.

photographic plate. The heads *E* and *F* were suitably ground and lubricated to make vacuum-tight joints. When required the two shutter halves could be raised and lowered together.

§ 4. THE VACUUM TECHNIQUE

The degree of vacuum required in the cathode chamber for the production of an electron beam of suitable velocity is of the order of 10^{-3} mm. Schobitz* has shown that in order to avoid loss of definition in the diffraction patterns the pressure in the diffraction chamber must be considerably less than 10^{-5} mm. In the instrument described above these conditions were fulfilled by means of the differential pumping system shown in figure 1. Whilst the 4-stage mercury-vapour pump was directly connected by a wide-bore (5-cm.) tube to the main body of the camera, the cathode chamber was evacuated through a 1.2-cm. bore tube *L*, the effective orifice of which could be reduced by means of the valve *V*. Since a steady flow of gas into the cathode chamber was maintained by means of the capillary leak system described elsewhere†, the conditions obtaining in the vicinity of the main evacuation port were similar to those of an injector. The arrangement proved so satisfactory, not only in the attainment of the necessary vacua but also in preventing diffusion of the mercury vapour into the camera, that it was found possible to dispense with a mercury-vapour trap.

The vacuum-tightness of the instrument depended upon that of thirteen flat lapped-surface joints ranging in external diameter between 4 and 15 cm. By experience it was found that the optimum width of lapped surfaces was about 2 cm., the surfaces being ground with coarse-grade carborundum paste on a steel surface plate. Whereas a more finely finished surface failed to hold the grease whilst under vacuum, the matt surface obtained by the above method prevented flow of grease. The grease was made by digesting 2 per cent of pure crêpe rubber in pure white petroleum jelly in vacuo in a boiling brine bath. Semi-permanent joints such as observation windows etc. were made with picein wax.

§ 5. PRODUCTION OF THE ELECTRON BEAM

For the purpose of accurate electron-diffraction analysis it is essential that the beam velocity and intensity be uniform during exposure. These requirements cannot be fulfilled by means of a hot cathode, because this would entail the use of a constant-voltage source of high tension. On the other hand, a cold-cathode discharge tube fed through a suitable current-controlling device offers a means for the production of a beam of steady current and voltage with a minimum outlay in smoothing equipment. Accordingly we have incorporated in our instrument a cold cathode fed through a diode operated under conditions of saturation. The high-tension condenser was filled to a peak voltage of 110 kV. by half-wave rectification of a 50 ~ transformer output. The maximum beam voltage employed in our experiments was 70 kV. The capacity of the condenser was such that with a discharge-chamber

* *Phys. Z.* 32, 37 (1931).

† *Loc. cit.*

current of 1 mA. the valve was still saturated throughout each idle half-cycle, the storage voltage never falling below about 90 kV. With a constant current flowing through the cold-cathode discharge chamber the beam velocity depended solely upon the gas pressure, which could be adjusted and maintained uniform over long periods by means of the capillary leak system.

§ 6. THE FOCUSING OF THE ELECTRON BEAM

The electron beam was focused in order to increase the ratio of beam to cathode-chamber current and the resolving power, and also to enable the beam to be separated from molecular rays. The first of these objects was attained by electrostatic focusing brought about by suitable design of the cathode chamber and diaphragm. In connection with this it is important to note that the diaphragm tube *M*, figure 1, protruded well into the cathode chamber and was shaped in such a manner as to subject the beam to an intense concentrating field. Whilst the bore of the diaphragm tube was 5 mm., its cathode-chamber end was spun down to an aperture of 0.1 mm. The beam issuing from the diaphragm tube was divergent, but could be rendered suitably convergent by means of the focusing coils. The following considerations lead to the conclusion, confirmed in practice, that the best results are to be obtained when the undiffracted beam is brought to a focus on or very slightly below the photographic plate. To fix ideas, consider a transmission specimen consisting of a film of randomly disposed crystals. Since the angle between incident and emergent paths of electrons of given velocity is constant for any set of Bragg planes, it is easy to see by a simple geometrical construction that a divergent beam will continue to diverge after diffraction, a parallel beam will remain parallel and, finally, a beam converging to a focus in the vicinity of, but rather below, the plate will result in the diffraction rings attaining maximum definition on a curved surface which is, with an effective camera-length of 50 cm., to all practical purposes coincident with the plate.

By means of levelling-screws the focusing coils could be tilted and the electron beam thus separated from the molecular rays, which could then be trapped and thus prevented from striking either specimen or photographic plate. Furthermore, by progressive tilting of the focusing coils the specimen could be rapidly and systematically explored.

§ 7. PROCEDURE

Two specimens, one for examination and the other for reference, were mounted side by side on the specimen-carrier, which was adjusted in such a manner that, when one specimen was in a suitable position in the electron beam, either simple rotation through 180° or a short predetermined horizontal traverse of the specimen-carrier would bring the second specimen into a similar position. The first half of the plate was then exposed, whereupon the second specimen was brought into the beam and the exposure completed on the second half of the plate. The whole operation could be completed in about 1 second. All conditions affecting the production of the electron beam were unchanged throughout these operations.

The reference specimen. The choice of the substance serving for the preparation of the reference specimen was governed by the following requirements. The specimen should (i) be easy to prepare in a reproducible manner for use in transmission or reflection; (ii) yield a large number of well-defined sharp rings, each of uniform intensity and without too pronounced a contrast of intensity between the rings; and finally (iii) consist of a substance the lattice constants of which have already been determined with great accuracy by X-ray diffraction. Specimens consisting of Pt, Au, Ag, Al, Mg, Zn, Cu, Fe, SnO_2 , PbO_2 , Al_2O_3 and ZnO respectively were examined for their suitability as reference materials. Of these, zinc oxide alone, prepared by the combustion of zinc vapour, fulfilled the necessary requirements. For the purposes of reflection the zinc-oxide smoke was deposited on a polished metal disc, whilst for transmission the oxide was collected on a fine-mesh nickel gauze. A number of such specimens were examined and the resulting diffraction patterns, of which that shown in figure 3 is characteristic, were so uniform as to establish clearly the reproducibility of the crystalline structure of specimens obtained in this manner. Six transmission and three reflection patterns were completely analysed. All planes within the range covered by the patterns were accounted for, and no forbidden rings occurred. Within the limits of experimental error inherent in previous methods of electron diffraction the values of the lattice constants obtained in each case agreed with the values given by Bragg* ($a = 3.220 \text{ \AA.}$; $c = 1.608$). In what follows all the measurements have been referred to these values, and in the event of their revision being found necessary it will be a simple matter to apply the appropriate correction to the results set forth below.

The preparation of the specimens of zinc oxide for examination, as distinct from those serving for reference purposes, will be described below.

§ 8. ANALYSIS OF THE DIFFRACTION PATTERNS

Analysis was carried out as follows. The reciprocals of the radii of the reference-pattern rings were plotted on a logarithmic scale and fitted to the suitable Hull and Davey† nomogram. In addition to identifying the rings in terms of the corresponding Bragg planes, this procedure also served to check the structure of the reference material. Spacings calculated from the accepted X-ray values were then assigned to the reference rings. Thereupon the rings due to the specimen under examination were measured by interpolation between adjacent reference rings and the corresponding Bragg-plane spacings calculated. The further procedure was as previously outlined.

It will be realized that the use of a reference pattern eliminates errors due to inaccuracy in measurement of accelerating voltage and effective length of the camera, together with those due to the photographic plate being flat instead of spherical about the point of diffraction. Distortion due to shrinkage in the emulsion of the plate and any lack of uniformity in the concentrating field in the planes at right angles to the undiffracted beam do not affect the measurements. Moreover it is

* *Phil. Mag.* 39, 647 (1920).

† *Phys. Rev.* 17, 549 (1921).

not necessary to assume the validity of de Broglie's law, but merely that a definite value of wave-length is to be associated with electrons of a given velocity. Since in all our experiments the beam was biased well away, usually about 5 cm., from its unfocused position, the occurrence of any change in the conditions associated with the production of the beam itself was betrayed by a displacement of one set of rings relative to the other. Figure 4 shows the effect produced by a small deliberate voltage-change between the two half-exposures. It will be seen that corresponding half-rings differ in diameter and are not described about a common centre. Furthermore, owing to its intensity at the photographic plate the beam of undiffracted electrons in many cases actually drilled a minute hole in the emulsion. Thus it was generally possible to tell at a glance whether a given plate should be retained for analysis or discarded.

§ 9. EXPERIMENTAL RESULTS AND DISCUSSION

In what follows, electron-diffraction patterns due solely to specimens of condensed zinc oxide crystallizing in a triangular close-packed lattice in the hexagonal system, with a basal axis of 3.220 Å. and an axial ratio of 1.608 and in which the crystal array was wholly random, are termed *reference patterns*, all others being referred to as *specimen patterns*. All patterns were obtained by transmission, the general plane of the diffracting film being normal, or nearly so, to the electron beam, unless otherwise stated.

The specimens were prepared by withdrawing a nickel wire loop 1 cm. in diameter from a skimmed melt of granulated zinc of forensic quality in a quartz crucible. A double-shutter photograph of the transmission patterns given by such a specimen and a normal zinc-oxide reference film is reproduced in figures 5 (A) and 5 (B), being the reference and specimen patterns respectively. In spite of the remarkable dissimilarity between these two patterns, the coincidence of certain rings in both is so exact as to enable the conclusion to be drawn that the specimen consisted, at least in part, of zinc oxide exhibiting the normal structure. The complete analysis of figures 5 (A) and 5 (B) is given below in table 1.

Thus, according to the analysis set forth in table 1, the specimen consisted of zinc oxide of normal crystal structure and lattice constants, together with zinc and zinc oxide basally pseudomorphic therewith. The relatively feeble intensities of the rings due to zinc and the pseudomorphic oxide strongly suggest that these substances were present in comparatively minute proportions, the specimens consisting for the most part of normal zinc oxide. Apart from the presence of rings due to such traces of zinc and pseudomorphic zinc oxide in the specimen pattern, the outstanding difference between figures 5 (A) and 5 (B) lies in the totally different distribution of intensities between the rings, and it was mainly owing to this disparity that W. L. Bragg and J. A. Darbyshire*, on obtaining electron-diffraction photographs essentially similar to that reproduced in figure 5 (B), assigned a face-centred cubic structure to films prepared in the manner outlined above.

* *Trans. Farad. Soc.* 28, 522 (1932).

Table 1

Zinc oxide reference		Partially oxidized zinc specimen			
Plane	Spacing d/N (Å.)	Spacing (Å.) obtained by inter- polation	Origin attributed to planes		
			Normal ZnO	ZnO basally pseudo- morphic with Zn	Zinc
—	—	3.79	(1.0.2) $\frac{1}{2}$	—	—
(1.0.0)	2.789	2.789	(1.0.0)	—	—
(0.0.1) $_2$	2.589	—	—	—	—
(1.0.1)	2.456	2.456	(1.0.1)	—	—
—	—	2.327	—	(1.0.0)*	(1.0.0)*
—	—	2.116	—	—	(1.0.1)*
(1.0.2)	1.897	1.897	(1.0.2)	—	—
—	—	1.722	—	—	(1.0.2)†
(1.1.0)	1.610	1.610	(1.1.0)	—	—
(1.0.3)	1.468	1.468	(1.0.3)	—	—
(1.0.0) $_2$	1.395	1.395	(1.0.0) $_2$	—	—
(1.1.2)	1.368	—	—	—	—
(2.0.1)	1.347	1.347	(2.0.1)	(1.1.0)†	(1.1.0)†
(0.0.1) $_4$	1.295	—	—	—	—
(1.0.1) $_2$	1.228	1.228	(1.0.1) $_2$	—	—
(1.0.4)	1.174	—	—	—	—
—	—	1.163	—	(1.0.0) $_2$ †	(1.0.0) $_2$ †
(2.0.3)	1.085	—	—	—	—
(1.2.0)	1.054	1.054	(1.2.0)	(1.1.4)	(1.0.1) $_2$
(1.2.1)	1.033	1.033	(1.2.1)	—	—
(1.1.4)	1.009	—	—	—	—
(1.2.2) $\frac{1}{2}$	0.976 $\frac{1}{2}$	0.976 $\frac{1}{2}$	(1.2.2) $\frac{1}{2}$	—	—
(1.0.5) $\frac{1}{2}$	0.971 $\frac{1}{2}$	0.971 $\frac{1}{2}$	(1.0.5) $\frac{1}{2}$	—	—
(1.0.2) $_2$	0.949	—	—	—	—
(1.0.0) $_3$	0.930	0.930	(1.0.0) $_3$	—	—
(1.2.3)	0.900	0.900	(1.2.3)	—	—
(3.0.2)	0.875	0.875	(3.0.2)	—	—
(1.1.0) $_2$	0.805	0.805	(1.1.0) $_2$	—	—

The lattice constants of the components of the partially oxidized zinc specimen, obtained by reference to normal zinc oxide of assumed constants, $a = 3.220$ Å.; $c = 1.608$, were as follows:

Pseudomorphic zinc oxide $a = 2.686 \pm 0.002$ Å.; $c = 2.56$.

Normal zinc $a = 2.686 \pm 0.002$ Å.; $c = 1.86$.

The origin of the faint innermost ring will be discussed below.

* Denotes a spot pattern superimposed on a ring.

† Denotes one or more spots due to the same set of planes.

‡ Signifies not resolved.

Now, it does not seem to have been realized hitherto that crystal orientation can under certain circumstances give rise to an abnormal distribution of electron-diffraction ring intensities without any splitting up of the rings into arcs. Owing to deep penetration, the intensity distribution between the rings in X-ray diffraction powder photographs is of great assistance in their analysis because the ring intensities may, as a rule, be taken as being proportional to the atom-densities in

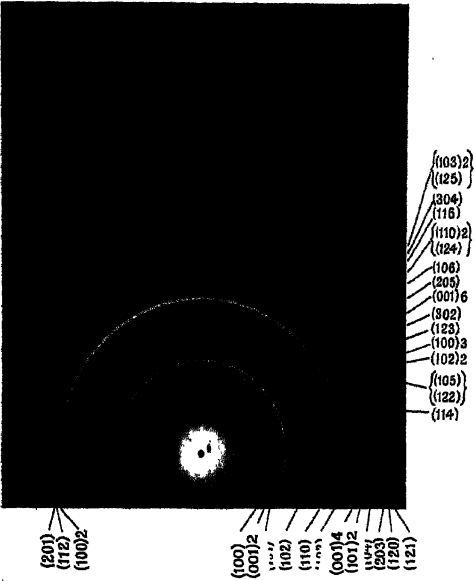


Figure 3. Normal zinc oxide.

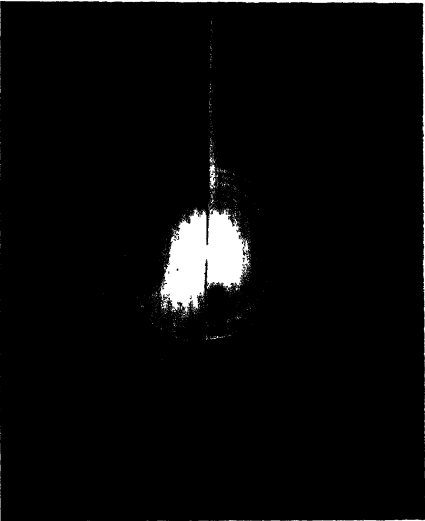
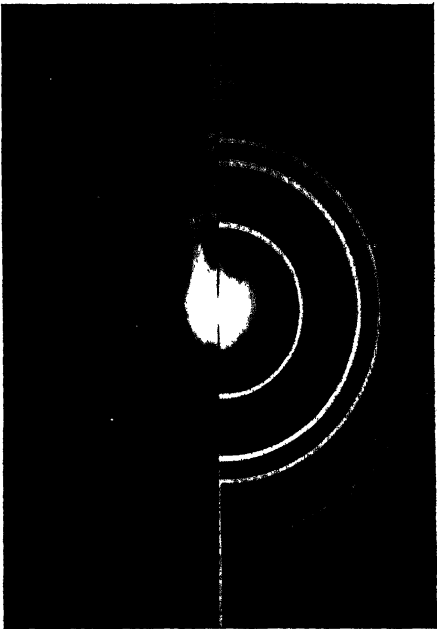


Figure 4. Faulty registration due to change in voltage.



A Reference pattern B Specimen pattern

Figure 5.

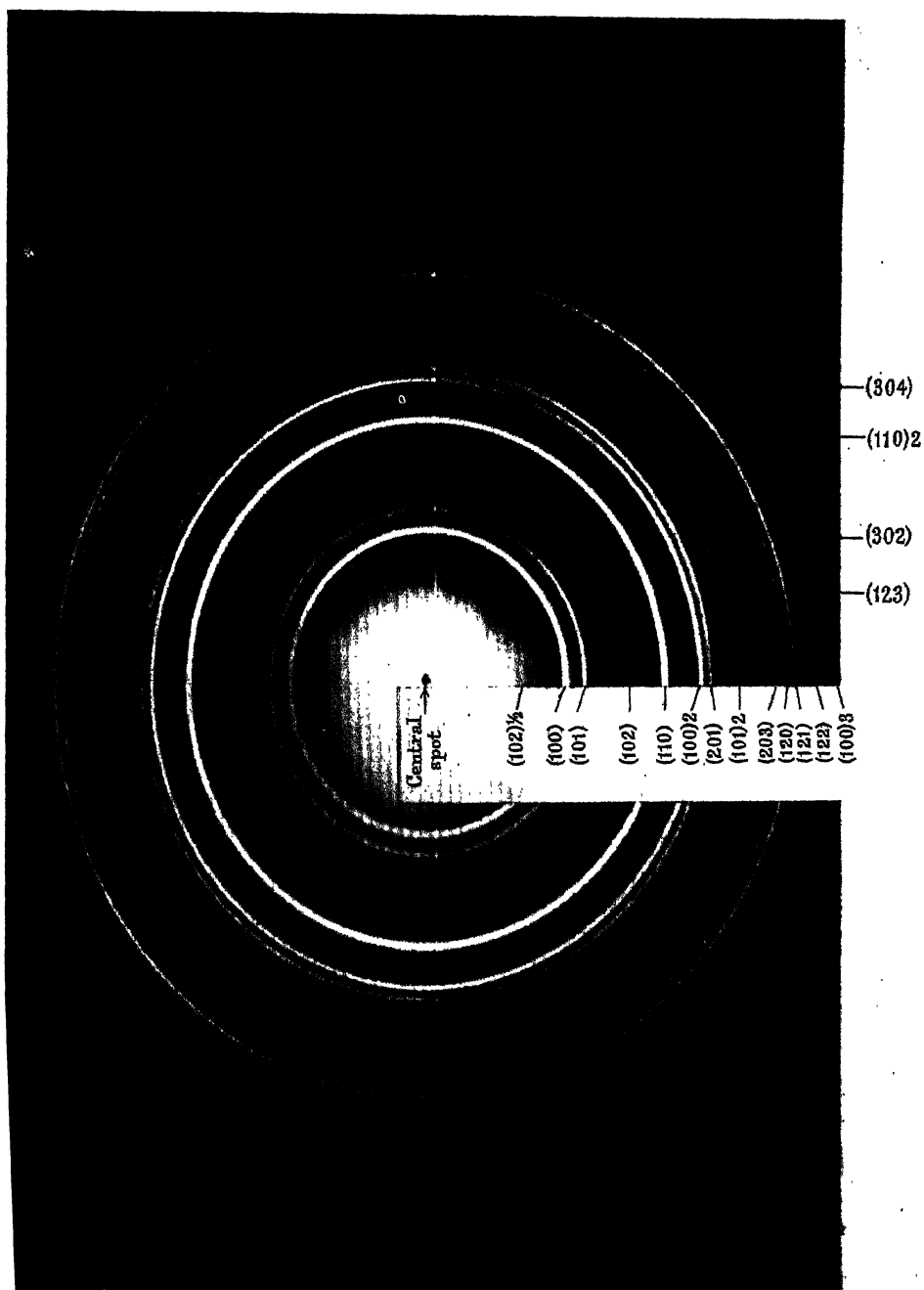


Figure 6. Normal zinc oxide formed by complete oxidation of a zinc film.

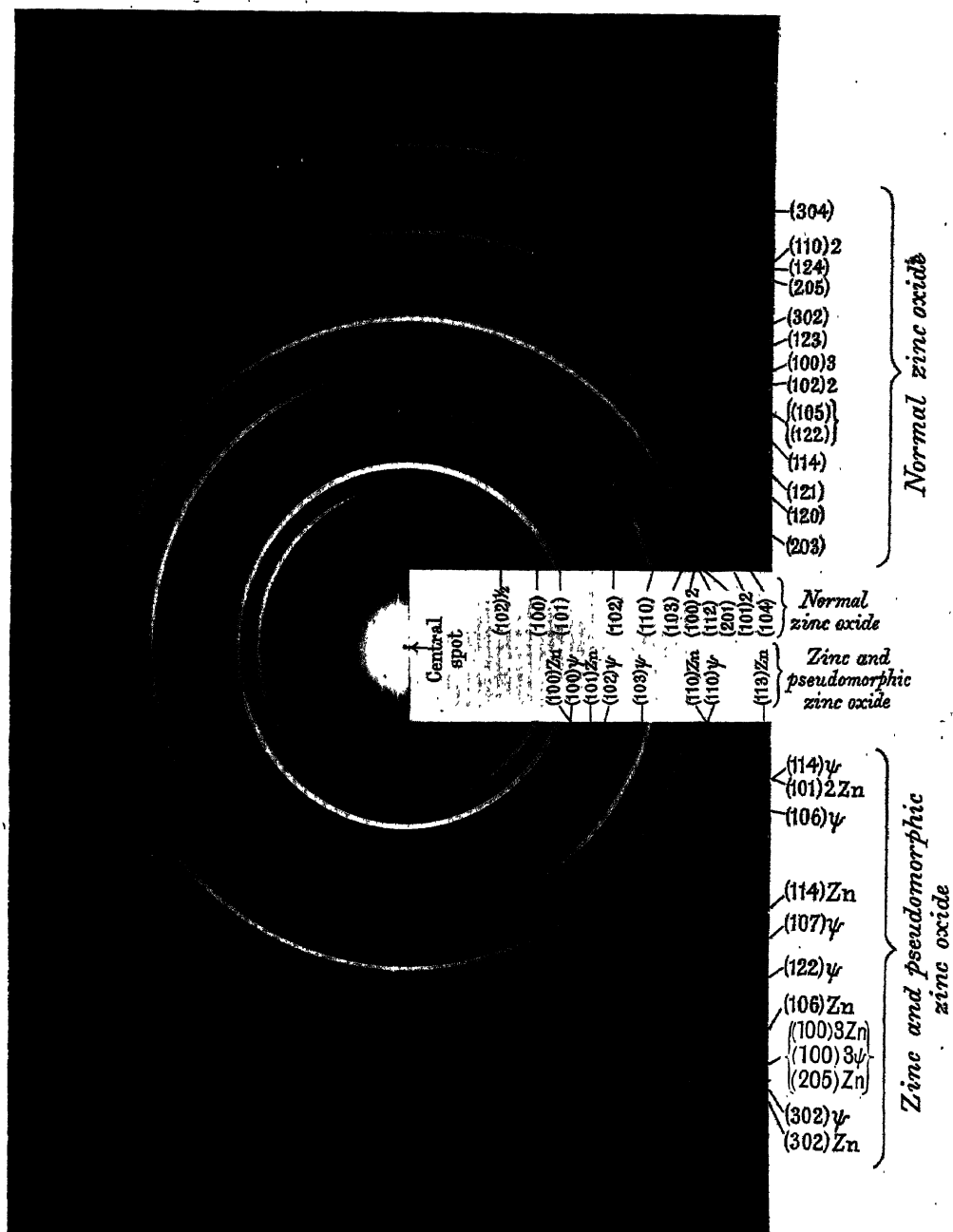


Figure 7.

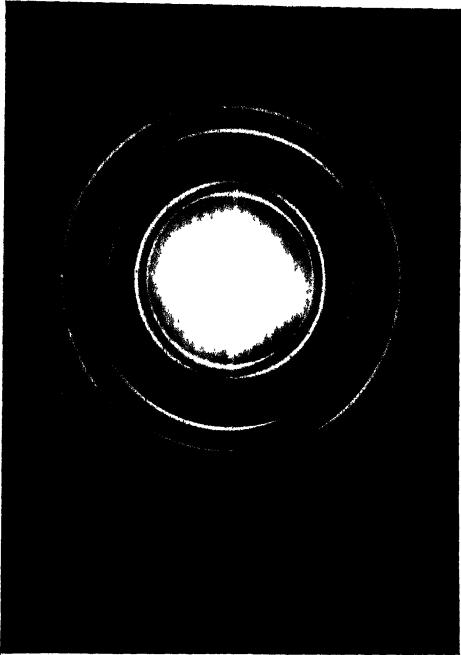
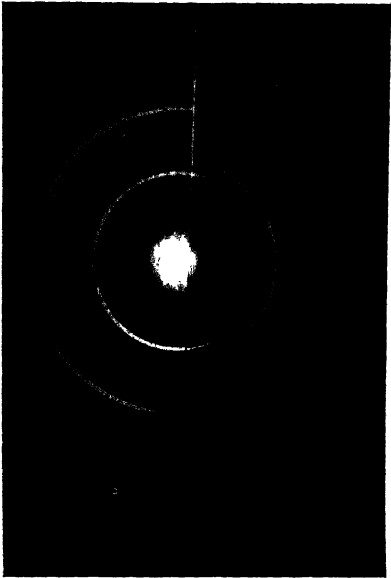


Figure 8.



A *B*
Figure 10.

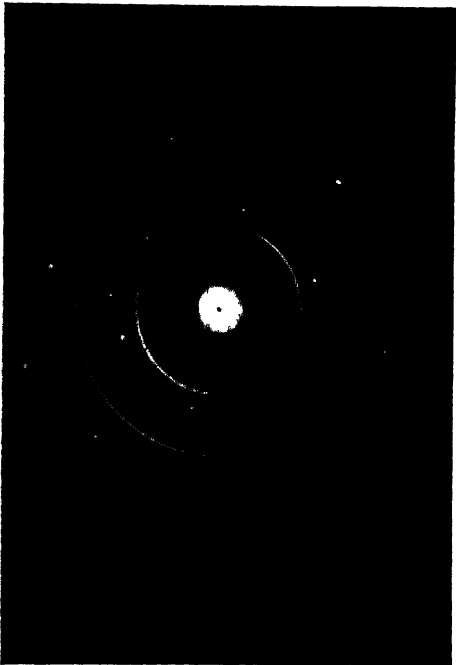


Figure 11.

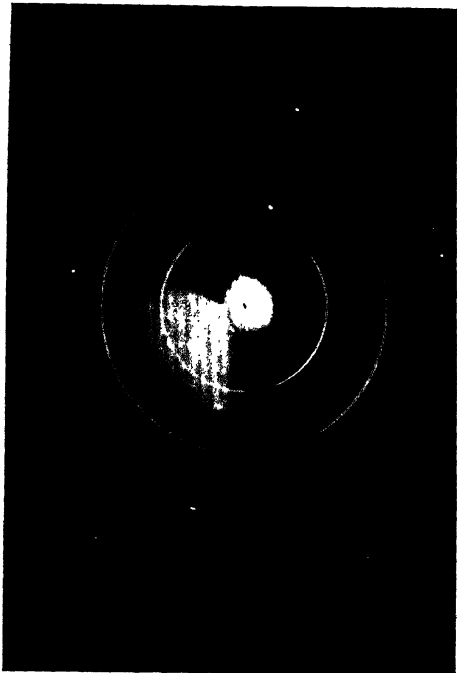


Figure 12.

the corresponding planes, and it seems to have been generally supposed that this practice can also be extended to electron-diffraction patterns provided that the rings are entire, i.e. of uniform intensity throughout each individual ring. Owing to the limited penetrating powers of the medium-speed (20 to 70-kV.) electrons usually employed, however, this is not permissible unless, indeed, it be already known that the crystals are randomly disposed. Consider, for example, a plane diffracting film consisting, to take the most symmetrical case, of cubic crystals orientated with two axes X , Y parallel to the film, but otherwise without constraint. Under these conditions reflection patterns will consist solely of spots forming a complete pattern indistinguishable from that given by a single crystal where it is rotated about a Z -axis maintained perpendicular to the plane of the film and therefore also normal to the electron beam. On the other hand, the corresponding transmission pattern obtained with the beam normal to the film will consist of complete rings of uniform intensity throughout each ring. The relative intensities of these rings, however, will differ from that produced by an array of randomly disposed crystals, in that only rings of zero third index will appear. Thus, the patterns will correspond to that given by a single crystal rotating about an axis coinciding with that of the electron beam. With gradual departure from an orientation perfect in the sense postulated, the reflection pattern will degenerate from spots into arcs, whilst hitherto absent rings will appear in the transmission pattern. In general, a plane polycrystalline film in which the directions of the crystals are random may be regarded in electron diffraction as equivalent to a single crystal exercising to the full both rotational degrees of freedom. All possible planes will be represented in the diffraction pattern, the relative ring intensities being proportional in the main to the atom-densities in the corresponding planes. Similarly, a film in which the crystals are orientated in a common direction may be treated as a single crystal with only one degree of rotational freedom and, if the axis of rotation coincide with that of the electron beam, the diffraction pattern will consist of complete rings formed solely by plane systems parallel, or nearly so, to the beam axis. Inclination of the rotational axis to the beam must result in the formation of a pure spot pattern. Finally, with the extreme degree of orientation we have, in fact, a single crystal devoid of both degrees of rotational freedom, and no matter what the directions of restraint may be a pure spot pattern will result. Thus, in electron-diffraction a spot pattern need not necessarily be due to a single-crystal structure, nor does a pattern of complete rings imply absence of orientation. Further, arcing of the rings, far from being a criterion of orientation, is rather to be regarded as evidence of imperfect orientation. Similar considerations apply to cases of lesser symmetry such as, for example, the hexagonal system.

In the light of these considerations it is now possible to put forward a reasonable explanation of the abnormal distribution of the ring intensities shown in figure 5 (B), and also in the patterns, figures 6, 7 and 8, obtained from other specimens prepared under approximately similar conditions. The normal zinc-oxide rings identified in these patterns, together with those of figures 5 (A) and (B), are classified in table 2 in order of decreasing steepness of their parent planes, together with the estimated

relative ring intensities. Also, where rings show a tendency to split up into arcs the approximate directions of arcing relative to that exhibited by the (1.0.0) ring are likewise recorded in table 2.

Table 2

Plane	Angle with basal planes (degrees)	Figure 5 A	Figure 5 B	Figure 6	Figure 7		Figure 8	
		Reference intensity*	Intensity	Intensity	Intensity	Arcs†	Intensity	Arcs
(1.0.0)	90	M	SS	SS	S	→	S	→
(1.1.0)	90	FM	SS	SS	MS	→	MS	→
(1.0.0) ²	90	F	S	S	FM	→	FM	→
(1.2.0)	90	VF	M	M	VF	→	VF	→
(1.0.0) ³	90	VF	M	F	VVF	→	VF	→
(1.1.0) ²	90	VF	F	F	VVF	→	Outside	range
(2.0.1)	75	F	M	M	FM	→	FM	→
(1.2.1)	72	VF	M	M	VF	→	F	→
(1.0.1)	62	MS	MS	MS	SS	↑	SS	↑
(1.0.1) ²	62	VF	Nil	VF	F	↑	VF	↑
(3.0.2)	60	VF	VVF	VF	VF	→	VF	→
(1.2.2)†	57	F	VF	VF	F	→	VVF	→
(2.0.3)	51	F	Nil	Nil	F	↑	F	↑
(1.2.3)	45	F	VF	VVF	F	↑	F	↑
(1.0.2)	43	M	VF	Nil	M	↑	M	↑
(2.0.5)	37	VF	Nil	Nil	VVF	?	Outside	range
(1.0.3)	32	M	VF	Nil	F	↑	VF	↑
(1.1.2)	30	M	Nil	Nil	M	↑	M	↑
(1.0.4)	25	VF	Nil	Nil	VVF	?	Nil	↑
(1.0.5)†	20	F	VF	VF	F	→	VVF	→
(1.0.6)	17	VF	Nil	Nil	Nil		Outside	range
(1.1.4)	16	VF	Nil	Nil	VVF	↑	VVF	↑
(0.0.1) ²	0	M	Nil	Nil	Nil		Nil	
(0.0.1) ⁴	0	VF	Nil	Nil	Nil		Nil	
(0.0.1) ⁶	0	VVF	Nil	Nil	Nil		Nil	

* The ring intensities are graded in order of increasing intensity as follows:

Nil—VVF—VF—F—FM—M—MS—S—SS.

† The arrows indicate the general directions of maximum arcing intensity.

‡ These two rings were unresolved.

All rings in figure 6 are due solely to normal zinc oxide, and their relative intensities are similar to those of the normal zinc-oxide rings in figure 5 (B). Thus, in putting forward an explanation of their relative ring intensities both patterns, figures 5 (B) and 6, can be considered together.

In the first place, rings due to planes of zero third index are, without exception, much more intense than the corresponding rings in the reference pattern, figure 5 (A), whilst rings of (0.0.z) type are completely absent, although in the case of the reference film the (0.0.1)² planes give rise to one of the most prominent rings in the normal pattern, figure 5 (A). In view of these facts it is difficult to resist the conclusion that, in the case of figures 5 (B) and 6, the specimen contained practically no crystals with the Z-axis in the plane of the film, i.e. normal to the electron beam,

and that a large proportion of the crystals were oriented in such a manner that their *Z*-axes were perpendicular to the film and thus parallel to the beam axis. Furthermore, though rings due to the (2.0.1) and (1.2.1) planes are likewise strengthened, the (1.0.1) rings in figures 5 (B) and 6 are approximately equal in intensity to the corresponding ring in figure 5 (A), whilst with still further decrease in plane steepness the specimen rings become progressively weaker than their reference prototypes. Thus it would appear that practically all the crystals in the specimens producing the patterns in figures 5 (B) and 6 were orientated between limits such that the inclination of the basal planes to the beam axis varied between about 60° and 120° , the great bulk of the crystals, however, being so orientated that this angle was 90° . These views are summarized in graphical form in figure 9, curve I. With

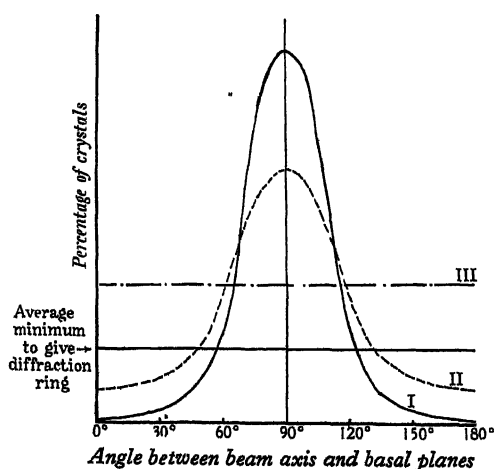


Figure 9.

decreasing extent of orientation the curve flattens out as shown in curve II until, with the random element complete, as in the zinc-oxide reference, the distribution is given by the straight line III. It will be appreciated that as the degree of orientation becomes less, diffraction rings will be observed from planes previously not in a position to diffract sufficiently to affect the photographic plate.

The patterns in figures 7 and 8 were obtained as previously with the general plane of the film normal to the electron beam. Nevertheless, they differ from figures 5 (B) and 6 as follows: (i) the rings show a tendency to break up into arcs; (ii) several rings missing from figures 5 (B) and 6 now appear; (iii) the zone of maximum increase in intensity as between reference rings, figure 5 (A), and specimen pattern rings, figures 7 and 8, has shifted from the region of the plane of zero third index to that of the (1.0.1) planes; and finally (iv) faint spot patterns are visible.

The pattern-changes (i), (ii) and (iii) suggest that whilst the general plane of the specimen was normal to the electron beam, either part or the whole of the film area actually examined was itself inclined to the electron beam at an angle of rather

less than 30° . This view is strongly supported by the observed directions of arcing recorded in table 2 and was confirmed experimentally by the double shutter record, figures 10 (A) and (B). In obtaining these patterns a half-shutter exposure, figure 10 (A), was first made with the specimen plane normal to the beam. The second half-shutter record, figure 10 (B), was obtained after the specimen had been rotated through an angle of approximately 30° about an axis lying in the plane of the film and passing through the point of impact of the beam axis with the specimen. The resemblance between figures 10 (A), 5 (B) and 6, and between figures 10 (B), 7 and 8, is such as to establish clearly the views set forth above.

The diameter of the innermost and usually extremely faint ring visible in all the specimen patterns excepting figure 8 corresponds to a Bragg plane spacing of 3.79 \AA . Although the directions of arcing of this and of the $(1.0.2)$ normal zinc-oxide rings are different, we can at the moment only suggest that the innermost ring is due to the half-order reflection from the $(1.0.2)$ planes of normal zinc oxide, the spacing of which is 1.897 \AA . It is significant that the intensity of this suggested half-order ring increases with increasing orientation of the normal zinc-oxide crystal bases in the plane of the specimen film.

The faint traces of spot patterns visible in figures 5 (B), 7, 8 and 10 proved on analysis to be due to both zinc and the pseudomorphic oxide. Further experiments were carried out with the object of obtaining specimens exhibiting more pronounced spot patterns. Such specimens were successfully prepared by slow cooling of films after withdrawal from the melt. To illustrate the results obtained it will suffice to reproduce the patterns, figures 11 and 12, obtained from one such specimen. The rings in both patterns are due to the normal form of zinc oxide. The spot patterns, however, are entirely due to zinc and zinc oxide basally pseudomorphic therewith.

The spot patterns in figure 11 must be due to a single crystal because all possible spots of the planes having zero third index are present, whilst no diffraction occurs from planes of $(0.0.z)$ type; this proves that the Z and electron-beam axes coincided. Owing to basal-plane pseudomorphism, spots due to planes of zero third index are common to both zinc and the pseudomorphic oxide. The specimen contained, however, other crystal fragments which were in a position to produce rings from such steep planes as the $(1.0.1)$ and $(1.2.1)$ of zinc and the $(2.0.1)$ of pseudomorphic zinc oxide. In the case of figure 12, the specimen plane had been rotated to make an angle of about 80° with the electron beam, with the result that some of the spots due to planes of zero third index have disappeared and others produced by less steeply inclined planes now appear. These results are set forth in detail in table 3.

A close scrutiny of the above and many similar diffraction patterns has failed to reveal any signs whatever of the existence of a zinc oxide with a structure intermediate between the normal and pseudomorphic forms. Nevertheless, it does not seem reasonable to suppose that the transition between the two forms occurs per saltum. It is much more probable that the change occurs in an exponential manner such that the amount of zinc oxide in the transition stage is so small as to have escaped detection.

Table 3. Analysis of the spot patterns in figures 11 and 12. Arcs and complete rings are due to normal zinc oxide and are not included in the analysis

Spacing d/N (Å.)	Figure 11		Figure 12	
	Zinc	Pseudomorphic zinc oxide	Zinc	Pseudomorphic zinc oxide
2.326	(1.0.0)	(1.0.0)	(1.0.0)	(1.0.0)
2.204	—	—	—	(1.0.1)
2.116	(1.0.1)	—	(1.0.1)	—
1.722	—	—	(1.0.2)	—
1.343	(1.1.0)	(1.1.0)	(1.1.0)	(1.1.0)
1.163	(1.0.0) ₂	(1.0.0) ₂	(1.0.0) ₂	(1.0.0) ₂
1.147	—	(2.0.1)	—	(2.0.1)
1.133	(2.0.1)	—	(2.0.1)	—
1.102	—	—	—	(1.0.1) ₂
0.907	(1.2.1)	—	—	—
0.879	(1.2.0)	(1.2.0)	(1.2.0)	(1.2.0)
0.872	—	—	—	(1.2.1)
0.861	—	—	(1.0.2) ₂	—
0.852	—	—	—	(1.2.2)
0.775	(1.0.0) ₃	(1.0.0) ₃	(1.0.0) ₃	(1.0.0) ₃

§ 10. CONCLUSION

In all, 42 patterns obtained from oxidized-zinc films and surfaces have now been examined in the course of the investigations outlined above and in a previous communication to the Royal Society*, with the result that certain facts have been established which suggest an explanation of the well-known corrosion-resisting properties of zinc. These facts may be summarized as follows: (i) When a zinc film is oxidized at room temperature in air, only the pseudomorphic modification of zinc oxide is formed; (ii) such pseudomorphic zinc-oxide films are sufficiently thin to be partially transparent to 40-kV. electrons; (iii) heating converts the pseudomorphic oxide into zinc oxide of normal structure which, however, is still separated from the metallic zinc by a freshly formed intermediate layer of pseudomorphic zinc oxide; (iv) when zinc appears in the form of a single crystal the pseudomorphic oxide does so likewise; (v) single crystal structure of the normal form of zinc oxide has so far not been observed in our experiments; and finally (vi) in the case of single-crystal films the hexagonal face invariably lies parallel, or nearly so, to the general plane of the film, and even in the polycrystalline films there is a pronounced orientation of a similar nature.

From its position in the periodic system zinc is a metal which might be expected to be peculiarly prone to atmospheric attack; but, as we have now shown experimentally, a fresh zinc film on exposure to air at room temperatures becomes covered with an extremely thin film of crystalline zinc oxide basally pseudomorphic with the zinc. The forces giving rise to the phenomenon of basal-plane pseudomorphism in this case also suffice to cause the pseudomorphic oxide to retain any

* *Loc. cit.*

single-crystal structure originally present in the case of the zinc film. The pseudomorphic zinc-oxide crystals in effect may be regarded as continuations of the zinc crystals, growing out of their hexagonal faces. These hexagonal faces tend to be orientated in the surface of the film. The atoms in the pseudomorphic zinc-oxide lattice are abnormally closely packed and thus difficult of penetration by oxygen, and the impenetrability by oxygen of the structure as a whole is assured by the pseudomorphic properties of the pseudomorphic zinc oxide and by the tendency of the zinc crystals to orientate themselves in such a manner that their hexagonal faces lie in the surface, conditions which all tend to ensure the formation of a completely continuous and, in the event of injury, self-healing film of pseudomorphic zinc oxide.

When zinc is oxidized at an elevated temperature the pseudomorphic oxide, which is stable at ordinary temperatures, is formed first and subsequently changed into the normal form of zinc oxide. Furthermore, since single-crystal films of the normal zinc oxide have so far not been observed by us, although such films of zinc and pseudomorphic zinc oxide were frequently obtained, it would appear that a single-crystal layer of pseudomorphic zinc oxide, in forming the normal oxide under the action of heat, disintegrates from a single crystal into a polycrystalline layer, owing to the considerable increase in basal dimensions accompanying the change from one modification of the oxide to the other.

§ 11. ACKNOWLEDGMENTS

We wish to thank the Cambridge Instrument Company, Ltd. for the gift of the electron-diffraction camera and the loan of a travelling microscope, Messrs Ferranti, Ltd. and Imperial Chemical Industries, Ltd. for grants and apparatus, and the Department of Scientific and Industrial Research for a grant which enabled one of us (A. G. Q.) to devote his whole time to this research.

DISCUSSION

Dr G. F. New. The results of this investigation are of interest in connection with the adhesion of oil paints to zinc surfaces. It is now apparent that the adhesion is in the first place to an oxide film instead of metal and this may explain the difficulties of producing satisfactory practical results. Although ordinary zinc oxide reacts with some types of linseed oil very strongly, it is possible that the pseudomorphic film of oxide is less reactive.

535.338.1:546.14.02

THE SPECTRA OF Br V, Br VI AND Br VII

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ABSTRACT. The vacuum spark spectra of bromine have been investigated under different degrees of excitation in the region λ 1400 to λ 400, by means of a Siegbahn spectrograph. From a careful scrutiny of the plates the lines have been assigned to the different stages of ionization of the element. With the aid of these the principal members of the spectra of Br V, VI and VII, involving the low-lying terms, have been identified.

§ 1. INTRODUCTION

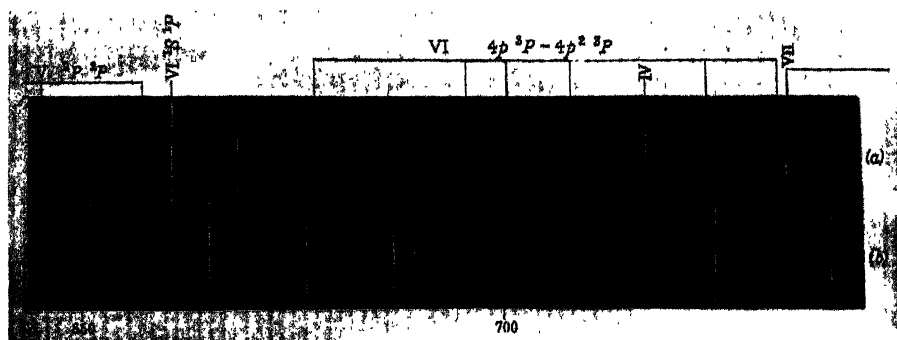
THE experimental observations that have hitherto been made on the spectrum of bromine in the extreme ultra-violet consist chiefly of those by L. and E. Bloch⁽¹⁾ who photographed the region between λ 6000 and λ 2200, using a high frequency electrodeless discharge through bromine vapour as their source. But the spectrum does not appear to have been investigated for series relationships below λ 1200, in which region many of the principal groups of the higher spark spectra of the element are expected to occur. With the exception of a few pairs of Br IX, we have no knowledge of the characteristics of these higher spark spectra. It is the purpose of the present paper to give an account of the regularities that have been discovered in the spectra of Br V, Br VI and Br VII, based mainly on a careful experimental study of the lines under different degrees of excitation in the vacuum grating region. An extensive use is made of the regular and irregular doublet laws in the location and detection of the chief multiplets in the above spectra.

§ 2. EXPERIMENTAL

The experimental work which formed the essential basis of the present paper was carried out by K. R. Rao in Prof. Siegbahn's laboratory at Upsala. The source used was a highly condensed vacuum spark between electrodes of Al tipped with the bromides of Cs and Rb. The intensity of the spark was altered by varying the capacity of the condenser from 0.27 μ F. to 0.09 μ F. and also by introducing an inductance of about 0.5 mH. into the secondary circuit. Photographs of the spectra of two different bromides helped in the identification of lines due to bromine itself. The vacuum spectrograph used was of the type designed by Prof. Siegbahn,

in which the grating was mounted at grazing incidence. The dispersion of the instrument is about 3.4 \AA./mm. at $\lambda 1400$ and about 2.4 \AA./mm. at $\lambda 400$. This large dispersion is necessary particularly in the case of bromine, which is extremely rich in lines in the vacuum grating region. The plates have been measured with the lines of O, N, C as standards. This comparison spectrum was superposed by changing the lower electrode to one of C or of Al tipped with LiNO_3 . Details of the method of exciting the spectrum and the method of evaluating the wave-lengths were fully dealt with in a former communication by one of the authors⁽²⁾. A portion of the spectrum between $\lambda 650$ and $\lambda 750$ is reproduced below.

Vacuum spark spectrum of bromine.



(a) Without inductance; (b) with inductance.

§ 3. THE SPECTRUM OF Br v

The spectrum of Br v is similar in structure to those of Ga I , Ge II , As III and Se IV and consists essentially of a simple doublet system. The important electron configurations and the resulting term structure are shown in table 1.

Table 1. Term scheme of Br v

3_1 3_2 3_3	4_1 4_2 4_3 4_4	5_1 5_2 5_3	Term prefix	Terms
2 6 10	2 I	I	4p	2P
2 6 10	2		5s	2S
2 6 10	2 I		4d	2D
2 6 10	2 I		4f	2F
2 6 10	I 2		4p ²	$^4P^2P^2D^2S$

By the application of the regular and irregular doublet laws to Ga-like atoms it has been possible to establish the important doublet combinations shown in table 2.

Table 2. Classifications in Br v

Combination	λ , with intensity in brackets	ν	$\delta\nu$
$4p^2P_2-4p^2^3D_2$	855.79 (1)	116851	
$^2P_2-^3D_3$	850.79 (8)	117538	687
$^2P_1-^3D_2$	813.40 (6)	122941	6090
$4p^2P_2-4p^2^3P_1$	657.60 (6)	152068	
$^2P_2-^3P_2$	645.49 (10)	154921	2853
$^2P_1-^3P_1$	632.30 (9)	158153	6085
$^2P_1-^3P_2$	621.11 (10)	161002	6081
$4p^2P_2-4d^3D_2$	549.81 (6)	181880	
$^2P_2-^3D_3$	547.94 (10)	182502	622
$^2P_1-^3D_2$	532.00 (10)	187970	6090
$4p^2P_1-5s^2S_1$	468.36 (5)	213510	
$^2P_2-^2S_1$	482.11 (10)	207422	6088

To avoid the use of fractions, an integral inner quantum number greater by half a unit than the true value has been assigned to each term of even multiplicity in the present paper. The above assignments are supported firstly by the behaviour of the lines. It has been definitely ascertained by a careful study of the various plates that they belong to Br v. Secondly the progressions indicated below in table 3 confirm the classifications made.

Table 3. Irregular doublet law applied to corresponding lines

Spectrum	$4p^2P_2-4d^2D_3$ ν	$\delta\nu$	$4p^2P_2-4p^2^2D_3$ ν	$\delta\nu$
Ga I	33961	42585	—	
Ge II	79246	35555	63412	19281
As III	114801	34430	82693	17640
Se IV	149231	33271	100333	17205
Br v	182502		117538	

Regular doublet law*

Spectrum	$4p^2P_1-4p^2P_2$	s	δs	$\delta^2 s$
Ga I	826	19.40		
Ge II	1768	17.96	1.44	0.55
As III	2940	17.07	0.89	0.22
Se IV	4376	16.40	0.67	0.15
Br v	6090	15.88	0.52	

* Cf. also K. R. Rao and J. S. Badami, *Proc. R.S. A* 131, 166 (1931).

Term values in the spectrum of Br v are given in table 4. The deepest term $4p^2P_1$ is given a value zero and the other values are based on this.

Table 4. Term values in Br v

Term	Term value	$\delta\nu$
$4p^2P_1$	0	
2P_2	6090	6090
$4p^2^3P_1$	158158	
3P_2	161011	2853
$4d^3D_2$	187970	
3D_3	188592	622
$5s^2S_1$	213510	

§ 4. THE SPECTRUM OF Br VI

The spectrum of Br VI, consisting of triplets and singlets, is isoelectronic with those of Zn I, Ga II, Ge III, As IV and Se V. In all these spectra the chief triplet and singlet terms have been identified. With the aid of the experimental data described in the previous section it has been possible to establish the combinations between the low-lying triplet and singlet terms of Br VI. The combinations identified in the present work are given in table 5.

Table 5. Combinations in Br VI

	$4p^3P_0$ 104316 2115	3P_1 106431	3P_2 111336 4905	1P_1 151274
$4s^1S_0$ 0	106431 (8) ? 939.57			151274 (10) 661.05
$4p^3P_0$ 244136 3270 3P_1 247406 6486 3P_2 253892	143100 (6) 698.81	137711 (6) 726.16 140981 (4) 709.31 147463 (5) 678.14	136070 (6) 734.91 142560 (8) 701.46	
$4d^3D_1$ 304648 319 3D_2 304967 484 3D_3 305451	200321 (4) 499.20	198210 (6) 504.52 198532 (8) 503.70	193315 (1) 517.29 193631 (8) 516.45 194115 (8) 515.16	

There can be no doubt as to the identification of the two triplet groups. For the choice of the singlet $4s^1S_0-4p^1P_1$, however, an alternative line is possible, namely $\nu 151154$ (10), but the behaviour of the two lines under different conditions of excitation favours the selection made in the above scheme, for the line $^1S_0-^1P_1$ is a resonance line and must appear under the weakest stimulus.

Table 6, which shows the application of the regular and irregular doublet laws to Zn-like spectra, supports the correctness of the above identifications. This table is an extension of similar sequences by Sawyer and Humphreys⁽³⁾.

Table 6. Regular doublet law

Term	Spectrum	$\delta\nu$	s	δs	δ^2s
$4p^3P$	Zn I	579.2	19.38		
	Ga II	1382	17.80	1.58	0.63
	Ge III	2403	16.85	0.95	0.25
	As IV	3677	16.15	0.70	0.16
	Se V	5210	15.61	0.54	0.12
	Br VI	7020	15.19	0.42	
$4d^3D$	Zn I	7.95	25.22		
	Ga II	65	22.91	2.31	0.96
	Ge III	179	21.58	1.33	0.55
	As IV	336	20.80	0.78	0.18
	Se V	550	20.20	0.60	0.23
	Br VI	803	19.83	0.37	

Irregular doublet law

Spectrum	$4p^3P_2-4p^3P_1$	$\delta\nu$	$\delta^2\nu$
Zn I	—		
Ga II	66472		
Ge III	84506	18034	559
As IV	101981	17475	336
Se V	119120	17139	189
Br VI	136070	16950	

In table 7 are given the term values in Br VI, based on the deepest term $4s^1S_0$ as zero.

Table 7. Term values in Br VI

Term	Term value	$\delta\nu$
$4s^1S_0$	0	
$4p^3P_0$	104316	
$4p^3P_1$	106431	2115
$4p^3P_2$	111336	4905
$4p^1P_1$	151274	
$4p^3P_0$	244136	
$3P_1$	247406	3270
$3P_2$	253892	6486
$4d^3D_1$	304648	
$3D_2$	304967	319
$3D_3$	305451	484

§ 5. THE SPECTRUM OF Br VII

The spectrum of Br VII like that of As V consists of simple doublets arising from the transition of the outermost *s* electron to the various excited states. Two pairs resulting from a combination between the low-lying doublet terms, $4s^2S$, $4p^2P$ and $4d^3D$ have been discovered. It was first definitely ascertained that the lines forming these combinations belonged to Br VII, by a close scrutiny of the plates. The pairs identified are given in table 8. The pair $4p^2P-5s^2S$ is expected to lie beyond the region investigated.

Table 8. Doublets of Br VII

Classification	λ (and intensity)	ν	$\delta\nu$	Term values
$4s^2S_1-4p^2P_1$	779.58 (8)	128274		$4s^2S_1 = 0$
$4s^2S_1-4p^2P_2$	736.09 (10)	135854	7580	$4p^2P_1 = 128274$
$4p^2P_2-4d^3D_2$	522.60 (0)	191351	861	$2P_2 = 135854$
$4p^2P_2-4d^3D_3$	520.26 (4)	192212	7579	$4d^3D_2 = 327205$
$4p^2P_1-4d^3D_2$	502.69 (4)	198930		$3D_3 = 328066$

As in the previous spectra, recourse has been had to the method of application of the X-ray laws to the sequence of Cu-like spectra to which the spectrum of Br VII

belongs. These regular progressions which are exhibited in the following table constitute excellent evidence of the correctness of the identification.

Table 9. Regular doublet law

Spectrum	$4p^2P_1-4p^2P_2$	s	δs	$\delta^2 s$
Cu I	248	20.19		
Zn II	873	18.23	1.96	0.79
Ga III	1718	17.06	1.17	0.38
Ge IV	2790	16.27	0.79	0.19
As V	4110	15.67	0.60	0.12
Se VI	5700	15.19	0.48	0.10
Br VII	7580	14.81	0.38	

Irregular doublet law

Spectrum	$4s^2S_1-4p^2P_1$	$\delta \nu$	$\delta^2 \nu$
Cu I	30535		
Zn II	48483	17949	1264
Ga III	65167	16684	544
Ge IV	81307	16140	312
As V	97135	15828	201
Se VI	112762	15627	115
Br VII	128274	15512	

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ON THE TILTED ELECTROMETER

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ABSTRACT. A detailed description is given of the construction and performance of a new, evacuated, critically damped, quick-reading, quartz-fibre electrometer. The sensitivity obtainable is limited only by the Brownian motion of the fibre. Photographic records are reproduced showing the response of the electrometer to suddenly applied potential-changes, and to the ionization currents of individual α particles. The minimum potential-change that can be measured (with the usual convention that the corresponding deflection of the system be not less than four times the root of mean square of the deflections of the Brownian motion) is of the order of 0.0001 V. when the period (undamped) is 5 seconds, and 0.0005 V. when the period is 1 second. The range of approximately constant sensitivity is adequate for most purposes.

§ 1. INTRODUCTION

AN improved model of the Wilson tilted electrometer^{(1),(2)} has been described in a previous paper⁽³⁾. This instrument had an outer airtight protecting case, and the design was arranged so that the tilting of the electrometer, the readjustment of the telescope, and the movements of the hanging leaf or fibre all took place about the same axis. It was stated that the instrument was reliable and very convenient to operate, that the range of approximately constant sensitivity and the stability of the instrument were for a given sensitivity much greater with a silvered quartz fibre hinged to the electrode by a piece of gold leaf than with a complete gold leaf, and that a somewhat higher voltage-sensitivity could be obtained with a fibre than with a gold leaf; but that the instrument responded inconveniently slowly at high sensitivity with either suspension. It was shown on filling the electrometer with hydrogen instead of air that this sluggishness was caused by the damping due to the viscous resistance of the gas.

An investigation has now been completed of the behaviour of this type of electrometer with the air damping of the fibre reduced and adjusted by a controlled evacuation of the air in the electrometer^{(3)*}.

It has been found, with a gold-sputtered quartz fibre of diameter about 10^{-4} cm. in the evacuated electrometer, that very high voltage sensitivities may be obtained, and that, when the motion of the fibre is critically damped, the time taken by the electrometer in responding to a potential change is remarkably short. The magnification that can with advantage be used is usually limited only by the Brownian motion of the fibre. The gold-leaf hinge which was inserted in the electrometer

* See the discussion, p. 185.

described in the previous paper is unnecessary with very fine quartz fibres, and is in fact disadvantageous on account of its comparative rigidity.

A new design for an electrometer, having all the advantages of the original one and in addition the advantage of simple construction, will first be described, and an account will then be given of the behaviour of the evacuated electrometer and of some essential details of the method of preparing and inserting suitable fibres.

It is evident that for rapid readings in the direct measurement of small electric charges the electrometer is superior to any of the well-known instruments. It is superior also in its general simplicity, and in the ease and rapidity with which its sensitivity may be changed.

§ 2. DESIGN

The electrometer, figure 1, was made of brass tube and plate of standard sizes, no castings being used. The joint *E* in the outer case, the quartz insulator *F*, and the glass insulator *G*, were made airtight with compressed rubber. The windows *H* were closed with good microscope cover glass sealed in position with a vacuum wax. The windows of the inner case could be left without glass but the fibre was

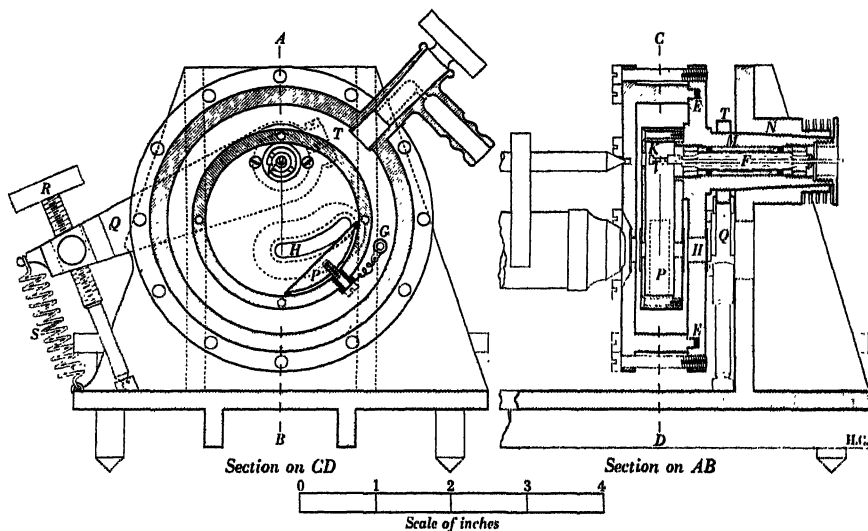


Figure 1.

then more liable to damage from any sudden change of the air pressure in the instrument. The employment of both an inner and an outer case was found to be absolutely essential for adequate protection of the fibre, even when the electrometer was evacuated. The whole instrument was supported by the axle *M* in the bearing *N*, and the tilt was adjusted with a long rigid lever *Q*, which was clamped to the axle. The end of this lever was controlled by a milled head screw *R* and a strong spring *S*. A preliminary rough adjustment of the tilt was obtainable by slackening the clamp *T*.

The positions of the plate *P*, and the point of suspension *V* of the fibre in the

electrometer case, were to a certain extent arbitrary, and for the purpose of reproduction were chosen so that the plate formed one side of a square inscribed in the case, and the axis V was on the diagonal of the square $\frac{1}{8}$ of its length from one end. Any improvements in the performance of the electrometer made by the use of a different disposition of the plate and of the fibre and by the introduction of a curved plate were found to be of quite secondary importance. The important factor was the type of fibre used (see below).

The best length for a given fibre in the electrometer, as was found by Kaye for gold leaves⁽²⁾, was the maximum length that could be employed without danger of the fibre touching the plate—in this model about 3 cm. Shorter fibres require higher plate voltages.

It will be seen that this electrometer is suitable for mounting directly through the wall of an ionization chamber by incorporating the bearing N , suitably modified, in the chamber wall.

The work about to be described was not carried out with this improved electrometer but with the original model of the instrument⁽³⁾, the only important difference being that the inner case of the older model was $\frac{1}{8}$ in. wider.

§ 3. GENERAL PERFORMANCE

The evacuation of the electrometer was found to produce no great improvement in its performance with a gold-leaf suspension. The time taken by the leaf to move to a new position of rest was, it is true, greatly reduced at the higher sensitivities, but the sensitivity of the electrometer was limited not so much by the damping of the leaf as by the extreme sensitiveness of the leaf to change in the tilt which is a characteristic of the electrometer with all suspensions when the range of approximately constant sensitivity becomes unduly short. Thus a typical leaf, using a microscope magnification such that 53 eyepiece scale-divisions corresponded to 1 mm., had a sensitivity of 500 divisions per volt over a range of only 4 or 5 divisions, and was then much too easily affected by any slight change in the level of the electrometer or in the shape of the leaf to have a constant zero-position. This sensitivity is about the maximum to be obtained with a gold leaf whether the electrometer is evacuated or not.

Further, very few of the gold leaves used were free from irregularities in their calibration curves. These irregularities, which must be well known to those who have used gold-leaf electroscopes, were either irregular changes in the slope of the curve or actual breaks where the leaf jumped suddenly to a new position without change in its potential. When the leaf was brought back, by means of a continuously variable potentiometer, over a range having one of these breaks, the return jump did not usually occur at the same leaf-potential as the former but somewhat later, so that the calibration curve had a kind of hysteresis loop. In regions removed from a discontinuity no hysteresis effects were observed with gold leaf.

A general description will now be given of the behaviour of the electrometer with a particular quartz fibre, which will be called "fibre no. 1." This fibre was

about 10^{-4} cm. in diameter and comparatively heavily (see below) sputtered with gold. It is to be noted that it was a fibre of medium quality, exemplifying both the advantages and some of the possible faults of these quartz-fibre suspensions.

When the sensitivity was adjusted to about 2000 divisions per volt, with the above-mentioned microscopic magnification, the instrument was found to be of little practical use when the enclosed air was at atmospheric pressure, because the fibre took many minutes to reach its new position of rest when a change of potential occurred. With a pressure of air in the electrometer, however, of 0.03 mm. of mercury, the motion of the fibre was critically damped, and it then took little more than 1 second to reach its new position. With a still lower air pressure in the electrometer the fibre oscillated before coming to rest. The most suitable air pressure to have in the electrometer at any sensitivity for most purposes is, of course, that at which the fibre is critically damped.

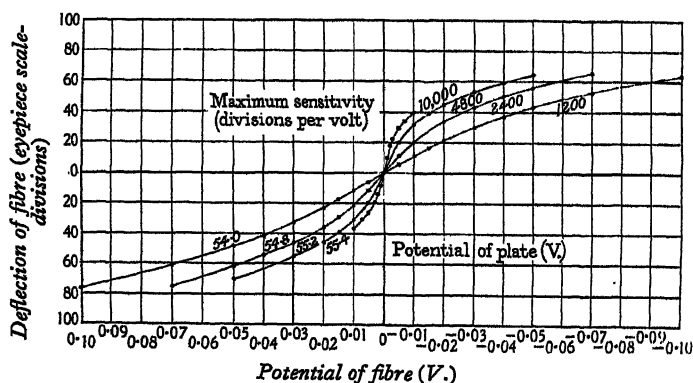


Figure 2. Fibre no. 1. Calibration curves at different plate-potentials.

The electrometer did not become unduly affected by slight changes in level till the sensitivity of the fibre had been raised to 10,000 divisions per volt, a sensitivity which is 20 times as great as that obtained with gold leaf. For the sake of completeness the calibration curves of fibre no. 1 are here given in figure 2. The calibration of the electrometer will be dealt with in detail in another section.

Another factor, which may have been either an elastic hysteresis or an electrical after-effect, influenced the performance of this fibre. The statement made above, that at 2000 divisions per volt the fibre took little more than 1 second to reach a new position of rest must be modified. It was found that a typical complete deflection of the fibre consisted of two parts, (1) a sudden initial deflection taking about 1 second, and (2) a creep over a small extra distance continuing for 2 or 3 minutes. This creep was least when the fibre was brought back to a potential from which it had been only momentarily changed, and was greater for a large deflection than for a small one. It was most troublesome at high sensitivity. It has been found (see below) that this defect in the performance of a sputtered quartz fibre in this electrometer can be entirely eliminated by sufficiently reducing the thickness

of the gold coating. It is of interest to notice that an after-effect very like this has been investigated by Israël⁽⁴⁾ in 12 models of the Lindemann electrometer⁽⁵⁾, manufactured by Spindler and Hoyer, Göttingen. He found that the needle after its first sudden excursion approached its final position exponentially and was usually very near to it after 5 minutes. He does not in that paper suggest a remedy for the fault.

A Cambridge falling-plate camera was now used to study the behaviour of this fibre. An image of the fibre was formed by a cinema projecting-lens with condensed light from a pointolite lamp. The beam of light on its way to the camera was reflected successively by two plane mirrors so that the shadow of the fibre on the front of the camera was vertical. Lines engraved at intervals of 1 mm. on the cylindrical lens in front of the camera slit produced a scale on the plates for displacements of the fibre, and a pendulum, near the lens, which cut off the light once a second, gave a time scale. The magnification was adjusted to be 53:1.

The manner in which the fibre oscillated about a new position of equilibrium, when the air pressure in the electrometer was much less than that required for critical damping of the fibre, is shown in figure 3, and the response of the critically damped fibre to suddenly applied potential-changes in figure 4. Thus, in figure 4, the trace at 500 mm./V. shows for the first 5 seconds the position of the earthed fibre. Then the potential of the fibre was changed to -0.01 V. and in less than 1 second the image moved about 5 mm. to a new position of rest. After 5 seconds the fibre was again earthed. Then -0.02 V. was applied for 5 seconds, and so on. The trace at 5000 mm./V. shows the adverse effect of the elastic hysteresis of this fibre.

The period of the fibre at different sensitivities was roughly measured from a series of photographic records of the type reproduced in figure 3. The air pressure in the electrometer was the same throughout the series, and was not low enough to allow many oscillations of the fibre at the higher sensitivities, but no correction was made for the effect of the damping on the period. The results are plotted in the upper curve in figure 5, which shows the measured period against the square root of the sensitivity. Substitution of the undamped period would make the curve more nearly linear.

The air pressures required for critical damping at different sensitivities of the electrometer were adjusted by running the Cenco Hyvac pump, which was used to evacuate the electrometer, against an air leak through a fine glass tube, and were measured by a Macleod gauge. A mercury-vapour trap was incorporated between the gauge and the system. The pressures ranged from 0.07 mm. of mercury at 500 mm./V. to 0.019 mm. at 5000 mm./V. When the logarithms of the pressures were plotted against the logarithms of the sensitivities all the points lay almost exactly on the same straight line. It will be observed that, on account of this change in the air pressure required for critical damping of the fibre at different sensitivities, the trace at the higher sensitivity in figure 5, where the range of constant sensitivity was not great (see figure 2), shows that the fibre was not critically damped for large deflections from zero.

There was a marked radiometer force on the fibre in the evacuated electrometer, particularly in the case of the strong illumination used for these photographs. If the pressure of the air and the intensity of the light were kept constant, however, the radiometer force had no adverse effect on the performance of the fibre. The trace reproduced in figure 6 shows the displacements of the zero position of the

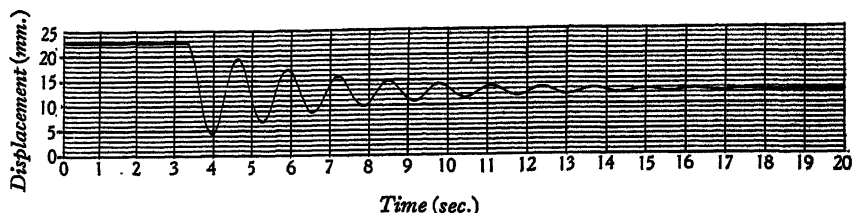


Figure 3. Period at 500 mm./V.

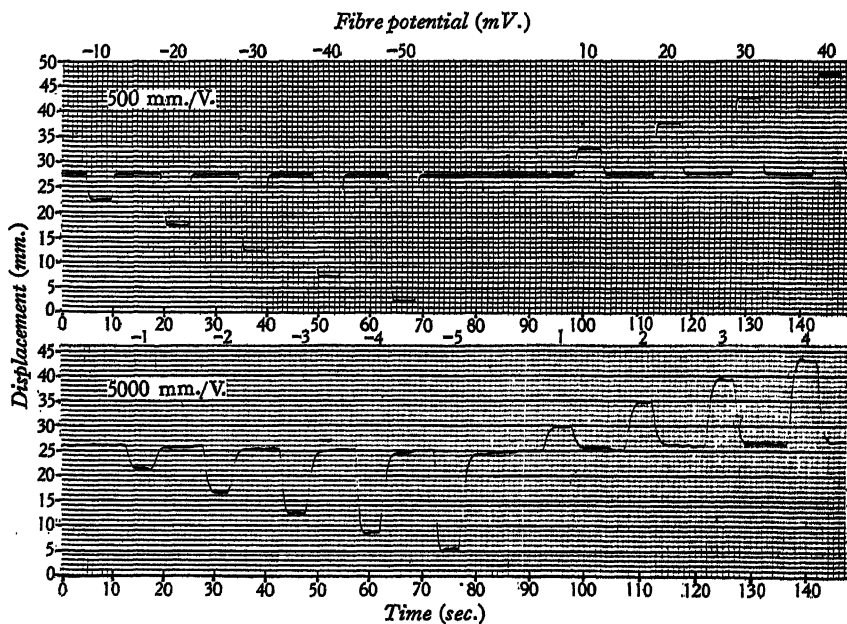


Figure 4. Response of the electrometer, fibre no. 1, to sudden potential-changes. The trace at 5000 mm./V. shows the adverse effect of sputtering a fibre too heavily.

earthed fibre, at a sensitivity of 2000 mm./V., brought about by putting pieces of plate glass suddenly into the beam from the pointolite lamp. The response of the instrument to a change in the intensity of the light is remarkably sudden.

In order to investigate the hysteresis found with fibre no. 1, and also in order to find whether the lightness of a quartz fibre was the factor which accounted for its superiority to gold leaf in the electrometer, experiments were made with a number of differently sputtered fibres. The result of these experiments can be deduced from the behaviour of the three fibres by which the experiments were

finally corroborated. These fibres will for reference be numbered 2, 3 and 4. They were cut from the same piece of quartz fibre of diameter between 0.001 and 0.002 mm., and were prepared as follows. Fibre no. 2 was sputtered for 1 hour. Fibre no. 3 was sputtered for 2 minutes over its whole length, and then for 1 hour over 1 cm. of its length, the rest being shielded. Fibre no. 4 was sputtered for 2 minutes only. The rate of sputtering was such that a coating of gold, which seemed to the eye to be as opaque as ordinary gold leaf, i.e. somewhat less than

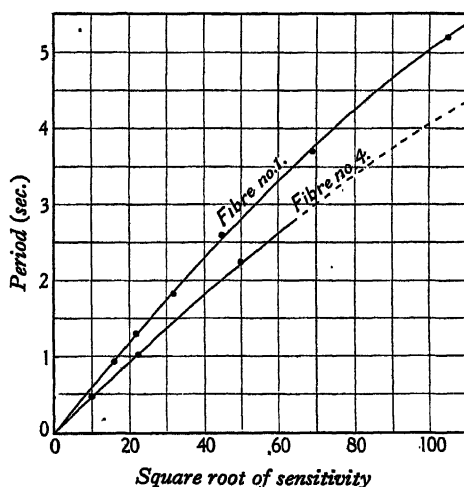


Figure 5.

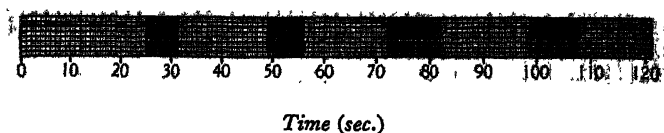


Figure 6. The radiometer effect: changes in the position of the earthed fibre produced by reducing the intensity of illumination with pieces of plate glass. Sensitivity 2000 mm./V.

10^{-5} cm. in thickness, was deposited in 1 hour on a flat glass plate placed in the sputtering apparatus.

The heavily sputtered fibre no. 2 was found to be quite useless. Its calibration curves, as far as they could be determined, corresponded to those of a gold leaf, and it had a comparatively quick initial response to a potential change, but the hysteresis effects were so great that it sometimes had to be kept near one position for more than a day before it stopped creeping.

Fibre no. 3 was inserted so that the heavily sputtered length was at the lower end of the suspension. The upper two centimetres, particularly the part near the electrode where most of the bending must occur, had thus a very thin coating of gold. No hysteresis was observed with this fibre, and in addition it responded

quite sharply to a sudden potential-change of the supporting electrode, which showed that the electrical resistance of the part of the fibre near the electrode was not too great, despite the thinness of the gold coating. On the other hand, on account of its weight, this fibre was inferior to a gold leaf in that the maximum useful sensitivity was less than 400 divisions per volt!

Fibre no. 4 was used for 4 months in the electrometer, and proved to be very satisfactory. The maximum sensitivity was found to be of the order of 12,000 eye-piece scale-divisions per volt (figure 9), and there were no hysteresis effects. The period was less than that of fibre no. 1, at any given sensitivity of the fibres, in the ratio of approximately 4:5 (figure 5), and was very much less than that of fibre no. 3 or that of a gold leaf.

As these three fibres were adjacent lengths of the same piece of fibre, and so would have performed similarly in the electrometer had they been similarly sputtered, the following conclusions can be drawn: (i) The after-effect with gold-sputtered fibres is caused by the gold coating and disappears if a thin enough film of gold is used; (ii) in this electrometer high sensitivity is obtainable when the weight of the moving part is small; and (iii) the period of the electrometer at a given voltage-sensitivity of the fibre is reduced by employing a lighter fibre. The behaviour of fibre no. 2 suggests that even the creep of long duration, often experienced at high sensitivity with the sensitive electrometers which employ a quartz fibre in torsion, may sometimes be caused by the metal film on the fibre.

§ 4. ADJUSTMENT AND CALIBRATION

The deflection of the fibre by alteration of the tilt at a fixed plate-potential V' will now be considered, the fibre and the case of the electrometer being at zero potential. If θ is the angle between the fibre and the vertical, and ϕ is the angle between the plate and the horizontal, as marked in figure 7 (a), then when ϕ is

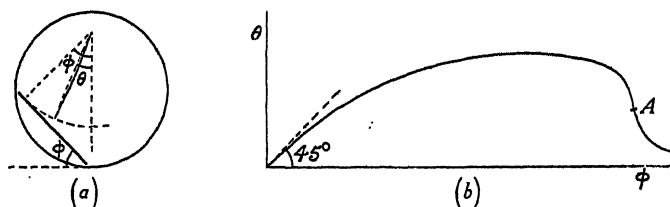


Figure 7.

small θ is approximately equal to ϕ , but as ϕ is increased the fibre tends to fall away from the plate and θ becomes less than ϕ . If the voltage V is not too great, θ reaches a maximum as ϕ is increased, after which it decreases more or less rapidly to small values, figure 7 (b). The fibre is found to be most sensitive to a change in its own potential at a point A on this curve where it is also most sensitive to a change in tilt. In using the electrometer, therefore, the fibre should be brought, by altering the

tilt, to the point A on one of these curves where the sensitivity of the fibre is constant over a certain range and is a function of the plate-voltage only. The deflection of the fibre at the point A will be called θ_A .

Two systems of these θ, ϕ curves are given in figure 8, one with plate-voltages 62, 64, 66 and 68 for fibre no. 3, and the other with plate-voltages 34, 36, 38 and 40 for fibre no. 4. The values of the tilt and of the plate-voltage in one of these systems of curves must not be too closely compared with the values in the other because these quantities are greatly dependent on the length of a fibre. The end of fibre no. 4 had an inherent curl, which was straightened out when the distance by which it cleared the plate was adjusted, and so it was effectively shorter than fibre no. 3. With a straight fibre, sputtered like fibre no. 4 and of rather smaller diameter, instability has been obtained with a plate potential of only 27 volts. Still finer quartz fibres could probably be prepared and inserted.

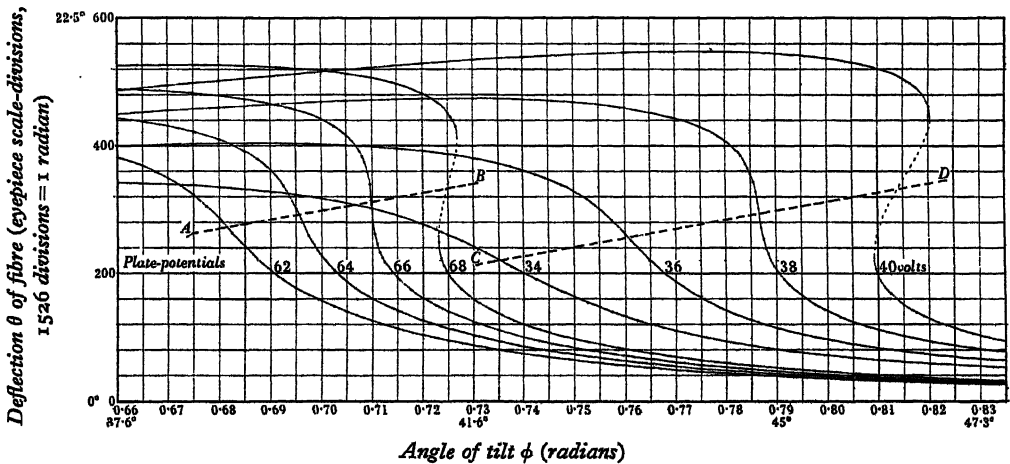


Figure 8.

The broken lines AB and CD , drawn through the points of greatest slope on these curves, are the loci of the deflections θ_A of the fibre, and of the positions of the microscope for maximum sensitivity in the middle of the eyepiece scale. If, however, the change in sensitivity is not great, so that θ_A does not change much, then the microscope does not require to be readjusted, and the operation of changing the sensitivity of the electrometer entails merely (i) alteration of the plate-potential to the value appropriate to the new sensitivity, and (ii) a corresponding change of tilt to bring the image of the zero potential fibre back to the middle of the microscope scale. The calibration curves in figures 2 and 9 have been taken with the microscope in a fixed position, and so show the magnitude of the error in the setting of the microscope to be expected when the sensitivity is changed in this way.

The curve at the highest plate-potential in each of the systems in figure 8 has a range of ϕ for which three values of θ are possible. At one of these deflections the fibre is in unstable equilibrium. The transition curve will have a critical point at which, theoretically, the potential sensitivity of the fibre will be infinitely great.

In figure 9 the fibre-potential calibration curves of fibre no. 4 have been treated in some detail. Three subsidiary graphs are given, showing (a) the change in the angle of tilt with sensitivity, (b) the change in the plate-potential with sensitivity, and (c) the length of the linear scale at different sensitivities. Curves (a) and (b) refer to the electrometer with the zero-potential fibre at the centre of the microscope scale, where all the curves intersect, and the changes in the tilt and in the plate-potential have been measured from the values at the critical point where the potential-sensitivity of the fibre would be infinite. To obtain curve (c) a "linear scale" was defined in the following way. A tangent to each calibration curve was drawn through its point of inflexion, and the length of the linear scale was taken to be such that at its ends the calibration curve differed from this tangent by 10 per cent of the displacement of the fibre from the point of inflection. The length of the linear scale was greater with fibre no. 4 at a sensitivity of 12,000 divisions per volt than with fibre no. 3 at 400 divisions per volt.

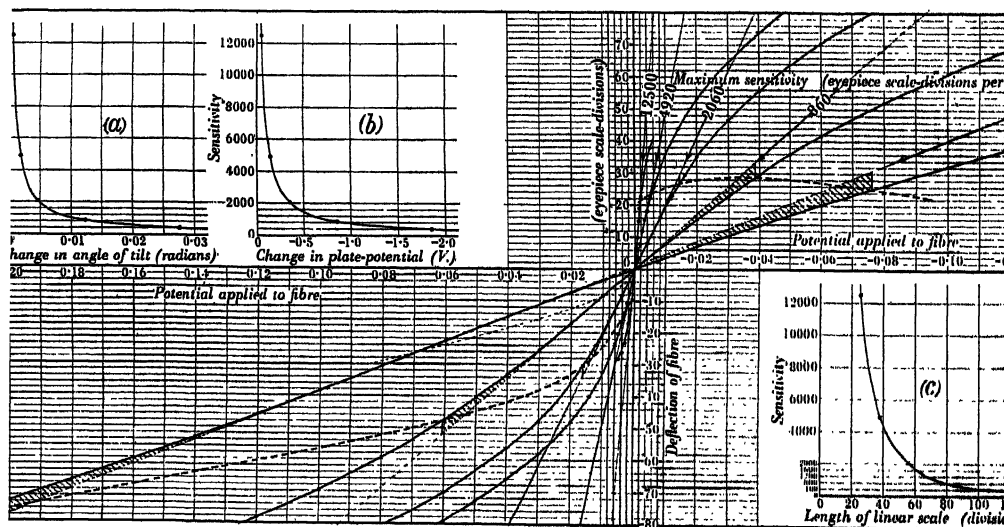


Figure 9.

The above calibration was carried out with a rather low optical magnification of the deflections of the fibre, namely 53 eyepiece scale-divisions to 1 mm., so that a large range of the sensitivity curves could be obtained without moving the microscope. The degree to which the sensitivity of the electrometer could be increased by the use of increased optical magnification of the fibre will be discussed in the next section.

The relation between the fibre-potential and the plate-potential sensitivity of the electrometer may be given. If the same small deflection of the fibre $\delta\theta$ is produced by a change of fibre-potential δV_F with the plate at constant potential V_P , and by a change of plate-potential δV_P with the fibre at constant potential V_F , it is found that $2\delta V_F = -\delta V_P$.

§ 5. LIMITING SENSITIVITY

It will be observed in figure 4, particularly at the higher sensitivity, that the fibre (no. 1) continually executed an irregular vibration about its mean zero position. It is evidently this motion of the fibre that imposes a limit upon the increase in sensitivity obtainable by increase of the optical magnification of the deflections of the fibre. The motion was not in the least reduced by placing the electrometer on a very stable concrete basement floor. It also remained unchanged in magnitude day and night, so that it could not have been caused by traffic vibrations from the streets. An irregular motion of the same kind, in the suspended system of the Hoffmann vacuum duanten-electrometer⁽⁶⁾, has been shown by Eggers⁽¹⁰⁾ to be the Brownian motion of the system, by the method of making from it a statistical calculation of Boltzmann's constant.

The equation of a harmonically bound system in Brownian motion is

$$R\bar{\phi}^2 = kT^{(8),(9)} \quad \dots\dots(1),$$

where k is Boltzmann's constant, T the absolute temperature, R the restoring couple of the system per unit angular displacement, and $\bar{\phi}^2$ the mean square angular deflection of the system from its mean position. In the absence of a mathematical theory of the electrometer analogous to that⁽¹⁰⁾ which Eggers used to enable him to evaluate R for substitution in this formula, it is not possible to repeat his work with the electrometer. The restoring couple R can, however, be eliminated, if the period P and the moment of inertia I of the fibre are introduced by the equation

$$P = 2\pi\sqrt{\frac{I}{R}} \quad \dots\dots(2).$$

The resulting equation is

$$\sqrt{\bar{\phi}^2} = \frac{\sqrt{(kT)} P}{2\pi\sqrt{I}} \quad \dots\dots(3).$$

By means of equation (3) it was very readily found that the above-mentioned motion of the fibre was the Brownian motion.

A rough measure of $\sqrt{\bar{\phi}^2}$ was obtained at a sensitivity of the electrometer of 2500 eyepiece scale-divisions per volt, with fibre no. 4, the microscope being adjusted so that 53 divisions corresponded to 1 mm. The readings of the position of the fibre, from which $\sqrt{\bar{\phi}^2}$ was calculated, were taken at intervals of 5 seconds, the magnification being increased by receiving an image of the fibre and the eyepiece scale on a graduated screen placed some distance away from the ocular of the microscope.

The value of $\sqrt{\bar{\phi}^2}$ was 1.0×10^{-4} radian, the period 2.2 seconds, and the absolute temperature 293°C . Using 1.4×10^{-16} erg/ $^\circ \text{C}$. per degree of freedom as the value of Boltzmann's constant, and substituting in equation (3), it is found that I is 5.0×10^{-7} gm. cm². Now this value of the moment of inertia of the fibre is the value obtained by assuming that the diameter is 1.5×10^{-4} cm., and that the mean density of the quartz and gold is 3 gm./cm³. A direct measurement of the diameter of the fibre was not made, but the fibre was taken from a batch of diameter "about

10^{-4} cm." supplied by the Cambridge Instrument Company, so that it probably was not in fact of much greater diameter than 1.5×10^{-4} cm. It is therefore evident that the greater part at least of the energy of this irregular motion of the fibre must be the equipartition energy of the Brownian motion. If the moment of inertia of the sputtered fibre were determined with some accuracy a measurement of Boltzmann's constant could readily be made by this method.

The minimum displacement which can be measured, under suitable magnification, in the case of a system executing the Brownian motion, is usually taken to be four times the root mean square of the Brownian displacements. The minimum voltage-change which can be read with the electrometer will therefore be, according to this convention, $4\sqrt{\phi^2}/S$, where S is the voltage-sensitivity of the fibre in angular deflection per volt. Now it has been shown experimentally, figure 5, that the period of the fibre is, for a given fibre, approximately proportional to the square root of the sensitivity, i.e.

$$P \approx A\sqrt{S} \quad \text{.....(4),}$$

where A is a constant. Therefore combining equations (3) and (4) we find that

$$\frac{4\sqrt{\phi^2}}{S} \approx \frac{4A^2\sqrt{(kT)}}{2\pi\sqrt{I}} \cdot \frac{1}{P} = \frac{B}{P} \quad \text{.....(5),}$$

where B is constant for a given fibre at a given temperature. Equation (5) shows that the minimum voltage which can be measured by the electrometer with a given suspension and sufficient optical magnification is approximately inversely proportional to the period.

It will be convenient, for purposes of comparison in the following table, to define a "limiting sensitivity" L of the electrometer such that

$$L = S/4\sqrt{\phi^2} \quad \text{.....(6).}$$

Table

Undamped period P (sec.)	Sensitivity S (mm./V.) Magnification $\times 53$	Limiting sensitivity L $\left(\frac{S}{4\sqrt{\phi^2}}/\text{V.}\right)$	Magnification for $4\sqrt{\phi^2}$ to give 1 mm.	10 % linear scale (mm.)
0.45	100	890	$\times 450$	—
1.0	500	1,970	$\times 200$	360
2.2	2,500	4,340	$\times 90$	90
5.0	12,500	9,860	$\times 42$	20

Thus L is the reciprocal of the minimum voltage which can be measured. The limiting sensitivity, with any given fibre, will be proportional to the period.

Some values of the limiting sensitivity of the electrometer with fibre no. 4 over a range of period from 0.45 to 5 seconds, are given in the table. The values were calculated according to equation (5) from the rough measurement of $\sqrt{\phi^2}$ at the period 2.2 seconds. The calculated values could not be properly verified experimentally at the two extremes of the range, on account of the difficulty of obtaining sufficient magnification at one end, and on account of the unsteadiness of the fibre

from causes other than the Brownian motion at the other end. It must be emphasized that near its maximum sensitivity the electrometer is of use only as a detector, unless very special precautions are taken to keep the tilt and the plate-voltage constant.

The table gives also the optical magnification that would be necessary to make $4\sqrt{\phi^2}$ correspond to a deflection of the image of the fibre amounting to 1 mm., and the length of the 10 per cent linear scale in mm. with this magnification. There is no doubt that it would be quite possible, with a lighter fibre in the electrometer, to reduce the restoring couple sufficiently for the Brownian motion to be observed with unit magnification, or in other words with the naked eye.

§ 6. MEASUREMENT OF CHARGE

No direct measurement has yet been made of the charge-sensitivity of the electrometer, but because of the very small capacity of the fibre itself, and the high potential-sensitivities which have been obtained, it is clear that the maximum charge-sensitivity must be high. It is probable that a charge of the order of magnitude of 1000 electrons could be detected without difficulty. If, in order to obtain a high charge-sensitivity, the electrometer were to be used in connection with an insulated system of very small capacity, it would be advantageous to modify the design given in figure 1 so as to reduce the dimensions of the electrode as much as possible. The bearing *N*, figure 1, could be arranged if necessary in front of the electrometer, a much shorter electrode being taken through the back.

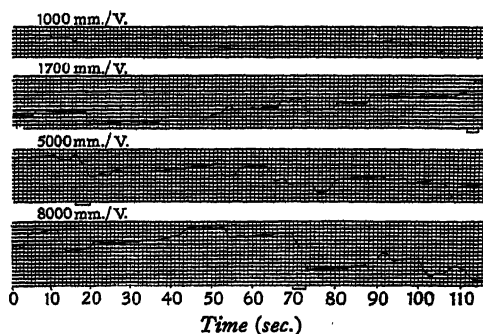


Figure 10. Potential-variations due to the natural leaks in two opposed ionization chambers filled with hydrogen, showing the ionizations due to individual α particles.

In figure 10 are some photographic records of the response of the electrometer (fibre no. 1) to the sudden ionization currents caused by α particles passing through hydrogen. The electrometer was connected to an insulated electrode of comparatively large capacity (total capacity of system 18 cm.) which passed into each of two ionization chambers. The cases of these were at potentials of + 300 and - 300 V. respectively. Traces of radioactive substances, which are always by nature present on the walls of the chambers and in the enclosed gas, gave rise to α particles, the more energetic of which would each produce about 10^5 pairs of ions in their passage through the gas. The currents across the chambers, resulting from these sudden

ionizations, were directed towards or away from the electrode according as the α particle occurred in the chamber with its case at the positive potential or in the other, and the sudden changes in position of the fibre, corresponding to the α particles, were on the average as frequent in the one direction as in the other. The sudden changes of position of the fibre were of the right order of magnitude to have been caused by ionization due to α particles, and it is not possible that they were caused otherwise than by ionization, because (i) after the potential-gradient across the ionization chambers had been removed, no large changes of position of the fibre were observed; and (ii) the sudden changes did not cease to occur when a resistance-capacity smoothing circuit, having a time-constant of about 50 seconds, was interposed between each ionization chamber and the battery used to maintain its potential. The movements of the fibre were found to be more sudden and of greater magnitude with hydrogen in the chambers than with air, carbon dioxide, or sulphur dioxide. These differences are probably accounted for by the different mobilities of the ions in the respective gases, and by greater recombination of ions in the heavier gases. The Hoffmann duanten-electrometer has been used by Ziegert⁽¹¹⁾ to measure the ionizations of individual α particles. The time taken by his instrument to register an α particle was, however, about 10 times as long as that required by this new electrometer.

When the ionization chambers described in the preceding paragraph were irradiated with X rays or with γ rays in such a way that the opposed ionization currents were on the average equal in magnitude, a very remarkable motion of the fibre of the electrometer was observed, similar in character to the Brownian motion of the fibre, but of much greater magnitude, except with very weak radiation. It was in fact easy to have the excursions of the fibre occupy the whole field of view of the microscope. No exact measurements have been made, but it is quite certain that this effect is due principally to the statistical fluctuations in the ejection of photoelectrons by the radiation. If, for example, it be assumed that each photoelectron ejected by a given radiation in an ionization chamber produces 10^3 pairs of ions in the gas in the chamber, and that the intensity of the radiation traversing the chamber is such that on the average 10^4 photoelectrons per second are ejected in the chamber, then the average current across the chamber is 10^7 electron charges per second and the root-mean-square fluctuation in this current, on account of the statistical fluctuation in the number of photoelectrons ejected by the radiation per second, will be $10^3 \times \sqrt{10^4}$ or 10^5 electrons per second, an amount of charge about equal to the ionization of an α particle and easily detected by the electrometer. This fluctuation will occur in both chambers, and the average currents being balanced out, the electrometer shows only the superposed fluctuations. As would be expected, the movements of the fibre become more vigorous as the intensity of the radiation is increased, and with X rays of different hardness but giving the same ionization currents in the chambers the fluctuations are greater for the harder rays.

All the well-known torsion electrometers, the Hoffmann⁽⁶⁾, the Compton⁽¹²⁾, the Lindemann⁽⁵⁾, and the Perucca⁽¹³⁾, employ a needle the moment of inertia of which cannot be reduced below a certain minimum, in view of the need for rigidity.

The great advantage of the principle of the tilted electrometer is that there is no such limit to reduction of the inertia of a hanging fibre, so that it enables a much shorter period at high sensitivity to be reached. A better performance, particularly in the measurement of charge, might be obtained by the use of a vertical fibre with two oppositely charged plates, either parallel to the fibre as in the string electrometer or oppositely inclined as in the Bumstead modification of the Wilson electrometer⁽¹⁴⁾, but simplicity, which is a feature of the Wilson electrometer, would then be lost.

§ 7. MANIPULATIVE DETAILS

The operation of inserting a fibre into the electrometer is difficult if a proper method is not followed, but the method which will now be described enables a new fibre to be mounted on a holder, sputtered, and inserted into the electrometer in less than an hour. There is no doubt that even simpler methods could be devised. The essential point in any method is that the lower end of the fibre be controlled until the inner case of the electrometer has been closed, and then set free after the fibre has been protected from air currents by the inner case. It is not possible to manipulate a freely hanging length of fine quartz fibre as one would a gold leaf.

A convenient form of holder for the fibre is shown in figure 11. The flat-sided spindle *K*, figures 1 and 11, is taken from the electrometer and fitted firmly into the holder as shown. Shellac to fix the fibre is applied at *K* and *L*, figure 11. The fibre is then brought up to the holder and the shellac softened by heating the holder with a small flame. Finally a small paper weight *M*, about 1 mm. square, is attached with seccotine near one end of the fibre. The distance *KM* is about 3.5 cm. Suitable fibres are supplied in 20-cm. lengths by the Cambridge Instrument Company. Four of these holders can be filled at one time by mounting them in line and bringing them into contact with a 20-cm. fibre.

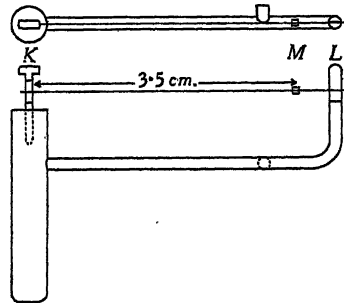


Figure 11.

For sputtering, the holder with its fibre is laid on a glass plate and placed under the gold plate of the sputtering apparatus. Then, after the holder has been fixed in a vice so that the fibre is vertical, the fibre is cut between *L* and *M* with a small pair of scissors, and the spindle *K* with the attached hanging fibre and paper weight is transferred to the electrometer. After the inner case of the electrometer has been screwed up, all that remains to be done is to cut the fibre to the correct length, allowing the paper weight to fall to the bottom of the case where it does no harm. The cutting is best done with a small pair of scissors through the front windows of the case. The plate should be charged to about 60 V. so that it will control the fibre after the latter has been cut. The lower edge of the window serves as a rest for the blades of the scissors and as a guide for the length of the fibre. The cut fibre when pointing directly to the plate should clear it by 1 mm. or less. If glass is used on

the windows of the inner case it is necessary to have a large hole closed by a plug in the round side of the case so that a pair of scissors with narrow blades can be inserted to cut the fibre.

Should the fibre when in use accidentally stick to the side of the case, it can always be set free, if the wall of the case is clean, by letting air very carefully into the electrometer and then giving the electrometer a violent to and fro rotatory motion about its axis, the plate being charged to about 60 V.

If difficulty is experienced in fitting a fibre which will move in the focal plane of the telescope, it may be necessary to substitute a narrow plate for the broad plate shown in figure 1. When this is done the plate-voltages necessary with a given fibre are higher and the calibration curves are not quite symmetrical, as in figure 2 where the plate used with fibre no. 1 was only 1/16 inch wide.

Earthing-keys using mercury or other liquids are not to be recommended. A dry clean brass-to-brass earthing key, totally enclosed in an earthed brass case and operating without friction, preferably by magnetic action, is satisfactory.

§ 8. ACKNOWLEDGMENTS

I am very grateful to Prof. Barkla for his supervision and for reading the paper, and to Mr Dymond for his interest in the work and in the paper. I acknowledge the benefit I have obtained from frequent discussions with Mr Stewart Brown, and I thank him for his collaboration in part of the work. I also thank Mr Mollison who has constructed some models of the electrometer for me according to the design given in this paper. The latter part of the work was carried out under the auspices of the Carnegie Trust for the Universities of Scotland.

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DISCUSSION

Mr R. S. WHIPPLE. The range of sensitivity covered by the instrument is very great, and I should like to ask the author whether, in practice, he finds that he is able to hold the vacuum sufficiently constant to obtain a good sensitivity over any length of time? This is not important if the instrument is being used as a detector, but if it is being used for measuring then it is essential that the vacuum be maintained constant.

I was interested to see that the author has found that a heavily sputtered fibre was almost useless. This has been our experience with the Lindemann electrometer. At the suggestion of Mr T. C. Keeley, we now sputter the fibres carrying the moving system in the Lindemann electrometer with the minimum amount of metal possible. In this way a fibre, instead of the fibre plus the metal coating, is able to keep control, and as a result much more reliable zeros are obtained.

Prof. A. F. C. POLLARD. In view of the several sources of energy-loss during motion of the fibre, I do not feel that the behaviour of the instrument has been fully investigated if the aperiodic hysteresis loop of instrumental variance, which would include with elastic hysteretic losses the unknown behaviour of the fibre end support, has not been plotted for the full range of the indications.

Mr J. GUILD suggested that it might perhaps be possible to make a solid solution of metal in fused quartz and thus avoid any undesirable effects that might arise from a coating of sputtered metal on the fibre.

Mr W. H. WHITE referred to the author's suggestion on p. 181 that it might become possible to see the Brownian movement with the naked eye, and pointed out that a fibre fine enough to give such large movements would itself be invisible.

AUTHOR'S reply. It is important that the air pressure in the electrometer be constant, especially if the fibre is strongly illuminated and a high sensitivity is being used, because under these conditions the displacement of the fibre due to radiometer forces is relatively large and it varies with the air pressure. I find, however, when the brass case of the electrometer is properly vacuum-tight and when good low-vapour-pressure wax is used to seal the windows and insulators, that in spite of the small volume of the case the vacuum is well maintained. It is very advantageous of course to increase the volume of the electrometer by connecting it to a large airtight vessel. Sometimes it is possible to make measurements, even if the electrometer is not airtight, by running the pump continuously, an adjustable auxiliary leak being used if necessary.

I wish to emphasize, in reply to speakers who have referred to the hysteresis, the fact that the metal coating on the fibre can be made so thin that hysteresis effects entirely disappear. It is therefore unnecessary to investigate in detail the aperiodic hysteresis loop of instrumental variance, since we know already that with a good fibre it is negligibly small.

When very fine fibres are used it is easy to arrange the illumination so that the fibre is observed against a dark background by means of the light which it diffracts.

I hope to publish soon some measurements of the charge-sensitivity of the electrometer.

A MECHANICAL WAVE MODEL ILLUSTRATING ACOUSTIC AND ELECTRICAL PHENOMENA

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ABSTRACT. A mechanical model is described which illustrates a band-pass filter. The model consists of a series of equal masses suspended on equal lengths of straightened watch-spring from a rigid bar. Through holes bored in the masses, which are equally spaced, is threaded a piece of elastic. One end is fixed, and the other can move with a simple harmonic motion, communicated by means of a rocker arm attached to a small motor. Wave-transmission along the system takes place only if the frequency falls within a certain range. Very high and very low frequencies are not transmitted.

The theory of the model is discussed, and various analogies to physical phenomena are pointed out.

§ 1. INTRODUCTION

THE problem of the transmission of a disturbance through a medium with resonant properties has always been of fundamental importance in physics, but it has more recently gained special interest as the result of the invention of acoustic and electrical filters, and also of the study of the Heaviside layer and the electrodeless discharge. It is natural, under these circumstances, to turn for illustration to some mechanical model where the vibrations are made visible.

So far as transmission along a uniform string is concerned, there is available, of course, the classical method of Melde. Sir Ambrose Fleming* extended Melde's experiment by replacing the fork by an electric motor with a rocker arm, and was thus able to show, in addition, the transmission of waves along a string loaded with beads. The author does not know, however, of any further experimental extension of this method.

§ 2. DESCRIPTION OF THE MODEL

The present model consists of a series of equal masses suspended on equal lengths of straightened watch-spring, so that each unit has a definite natural period. Through holes bored in the masses is threaded a piece of elastic, such as is used for toy aeroplanes, and the whole system therefore gives the appearance indicated in figure 1.

The springs are clamped at the top by a rigid metal bar and are equally spaced. One end of the elastic runs over a pulley, and the other is attached to a rocker arm coupled to a small electric motor. The rocker consists of a light pivoted rod kept

* *Proc. Phys. Soc.* 26, 61 (1913). Note also in this connection the well-known model of Vinycomb (Griffin and Tatlock, Ltd.).

in contact with the edge of an eccentrically mounted brass disc by means of a spring. The rocker, when in action, thus communicates to the string, in a horizontal line at right angles to its length, an approximate simple harmonic motion. The speed of the motor is recorded by a tachometer and is controlled electrically by a potentiometer resistance, or mechanically by a continuously variable gearing of a simple kind. In this way, vibrations ranging from about 3 to 20 periods/sec. are obtainable.

§ 3. GENERAL DISCUSSION OF THE ACTION OF THE MODEL

When very slow vibrations are applied to one end of the string, it is noticed that the nearest masses vibrate, but that the amplitude of vibration rapidly decreases from mass to mass. Nothing of the nature of ordinary wave transmission takes place.

With increase of speed of the motor, however, a certain critical speed is reached when a sudden change sets in. Waves travel freely along the string, and may form stationary systems. Finally, when a high speed is reached, wave transmission ceases again, and the vibrations die out at a short distance from the spot where they are initiated. The refusal of the system to transmit high-speed oscillations is very striking.

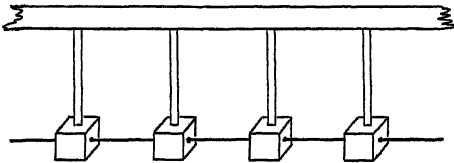


Figure 1.

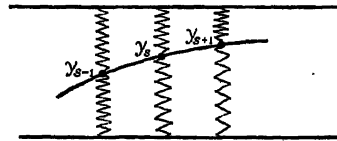


Figure 2.

In order to understand the interesting features that the model thus displays, it is necessary to consider the equations of motion.

Suppose the elastic is of unlimited length, and let T be its tension. Let m be the mass of each load, and a their distance apart. Let y_s be the displacement of the s th mass, and k^2 the restoring force due to the spring per unit displacement. (In figure 2 the springs are represented as spirals merely for the sake of the diagram.)

We thus have

$$m \frac{d^2 y_s}{dt^2} = T \left(\frac{y_{s+1} - y_s}{a} \right) - T \left(\frac{y_s - y_{s-1}}{a} \right) - k^2 y_s \quad \dots\dots(1),$$

and we require the solution of this equation subject to the condition that the first mass moves with a simple harmonic motion. If we decide further to consider only the steady state, then any other mass must also move with a simple harmonic motion of this same period.

Clearly there are three solutions that concern us, but the one that relates to the free transmission of waves is the simplest to begin with.

$$\text{Let} \quad y_s = Y \cos (pt - qsa) \quad \dots\dots(2)$$

be tried as a solution, where $p = 2\pi n$, n being the frequency, $q = 2\pi/\lambda$, λ being the wave-length, and where Y is the maximum displacement.

By substitution in (1) we find, on reduction,

$$-mp^2 = \frac{2T}{a} (\cos qa - 1) - k^2 \quad \dots\dots(3).$$

Provided, therefore, that we satisfy this condition, (2) will be a solution.

Rewriting (3) in terms of n and λ we have

$$n = \frac{1}{2\pi} \sqrt{\left(\frac{4T}{ma} \sin^2 \frac{\pi a}{\lambda} + \frac{k^2}{m}\right)}.$$

It is clear that n must be kept between the limits

$$\frac{k}{2\pi\sqrt{m}} \quad \text{and} \quad \frac{1}{2\pi} \sqrt{\left(\frac{4T}{ma} + \frac{k^2}{m}\right)}.$$

In the former case $\lambda = \infty$, and in the latter case $\lambda = 2a$. Within these limits therefore (2) is a solution.

Consider now the case when the vibrations imposed on the first mass are very slow. The apparatus shows, as has already been pointed out, that the amplitudes of vibrations of succeeding masses diminish rapidly, and it is perhaps natural therefore to try a solution of the type

$$y_s = Y e^{-K_1 s a} \cos pt \quad \dots\dots(4),$$

where K_1 is a constant.

This on substitution in (1), and after reduction, gives

$$-mp^2 = \frac{2T}{a} (\cosh K_1 a - 1) - k^2,$$

$$\text{or} \quad \cosh K_1 a = 1 + \frac{ak^2}{2T} - \frac{4am\pi^2 n^2}{2T} \quad \dots\dots(5).$$

Since the hyperbolic cosine of an angle varies from 1 to ∞ , we can satisfy (5) provided $n \leq k/2\pi\sqrt{m}$, and (4) is therefore a solution for the range from this value of n , to $n = 0$.

It now remains to consider the range above the value

$$n = \frac{1}{2\pi} \sqrt{\left(\frac{4T}{ma} + \frac{k^2}{m}\right)}.$$

Here no obvious solution suggests itself. The wave dies out as before, but the possibility of combining an exponential and a cosine term has already been exhausted. It will be shown later that the model itself suggests the type of solution required, but admittedly it does this much more easily when we know the result in advance. I am indebted therefore to my mathematical colleague Mr Wright for directing me to, and amplifying, a valuable source of information* where a similar problem relating to pendulums connected with springs, together with the whole subject of linear difference equations, is discussed.

The modification to (4) necessary to make it apply to the highest frequencies is simple. In fact only a multiplication by $(-1)^s$ is necessary, so that we can now write

$$y_s = Y(-1)^s e^{-K_1 s a} \cos pt$$

* Bateman, *Partial Differential Equations of Mathematical Physics*, p. 233. See also a paper by T. B. Brown, *J. Opt. Soc. America*, 8, 343 (1924).

and this, on substitution in (1), gives on reduction

$$\cosh K_2 a = \frac{4am\pi^2 n^2 - ak^2}{2T} - 1 \quad \dots\dots(6).$$

Since again the hyperbolic cosine of an angle varies from 1 to ∞ we can satisfy (6) provided

$$(4am\pi^2 n^2 - ak^2)/2T > 2,$$

i.e. provided $n > \frac{1}{2\pi} \sqrt{\left(\frac{4T}{ma} + \frac{k^2}{m}\right)}$, which is the range we want.

Hence we have three solutions:—

From $n = 0$ to $n = k/(2\pi\sqrt{m})$, $y_s = Ye^{-K_1 sa} \cos pt$;

from $n = k/2\pi\sqrt{m}$ to $n = \frac{1}{2\pi} \sqrt{\left(\frac{4T}{ma} + \frac{k^2}{m}\right)}$, $y_s = Y \cos(pt - qsa)$;

from $n = \frac{1}{2\pi} \sqrt{\left(\frac{4T}{ma} + \frac{k^2}{m}\right)}$ to $n = \infty$, $y_s = Y(-1)^s e^{-K_2 sa} \cos pt$,

and the whole range is thus covered.

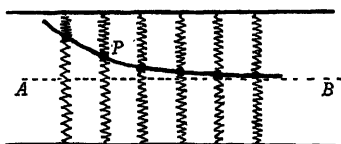


Figure 3.

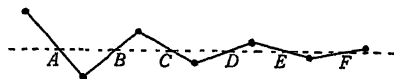


Figure 4.

These solutions represent satisfactorily the features the model exhibits, but it is possible to obtain much information in a general way, and thus further to interpret the results.

If a simple harmonic motion of frequency lower than the critical frequency is imposed on the end load, then, in the steady state, any load near by, say P , figure 3, must also vibrate with this frequency.

In order that this may happen, the restoring force must be less than that due to the spring alone and therefore the string must exert a force in opposition. Hence the string must always present a convex face to the central line AB , and thereby hold back the masses. No wave transmission, therefore, is possible. The solution $y_s = Ye^{-K_1 sa} \cos pt$ exhibits the exact shape of the convex curve from time to time.

Let the frequency of the impressed simple harmonic motion be now increased until it reaches that of one of the loads on a spring. Then again, in the steady state, P will vibrate with this frequency, but this will only be possible if there is no interference from the string itself. Hence all the masses must move backwards and forwards in phase, and the string will be straight. It could be said, in fact, that a wave of infinite length was being transmitted. For the transmission of a higher frequency, it is necessary that the restoring force due to the springs should be aided by the string itself. The latter must therefore, in the displaced position, always be concave to the central line AB . The curve $y_s = Y \cos(pt - qsa)$ achieves this.

As the frequency imposed on the end load increases, so does the concavity of

the string; in other words the waves become shorter and shorter. A further transition is reached, however, when the half wave-length is equal to the distance between the masses. Each mass now vibrates in such a way that the half-way points between it and the adjacent masses remain fixed. A mass can vibrate still faster, however, if the fixed points are arranged as in figure 4 at *A, B, C, D, E, F*, so that the mass is nearer to one fixed point than to the other. Here it is clear that the restoring force on each mass is greater than before, but the result is only secured by an ever diminishing amplitude. The solution

$$y_s = (-1)^s Y e^{-K_1 s a} \cos pt$$

is an analytical representation of figure 4.

Clear general ideas may thus be obtained of the working of the model.

§ 4. QUANTITATIVE EXPERIMENTS WITH THE MODEL

The region that lends itself most to experiment is the transmission band. The limit, on the high-frequency side, should be the frequency of a complete element

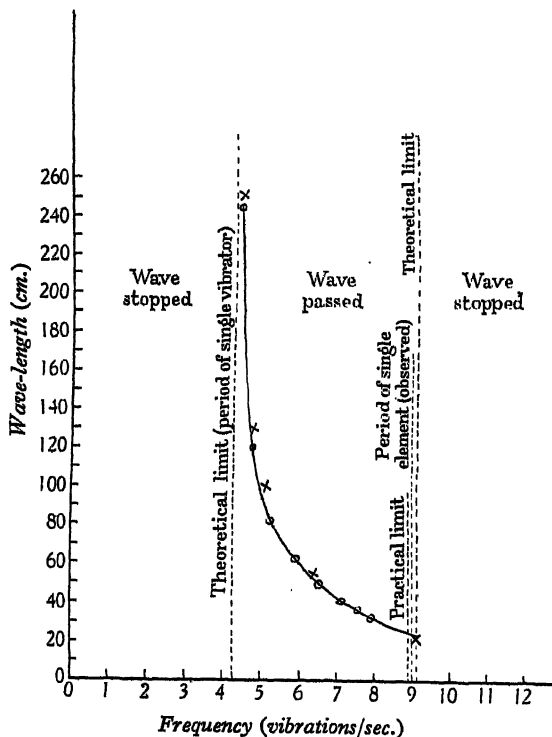


Figure 5. Band-pass filter. Average mass of vibrator, 14 gm.; average frequency of vibrator, 4.3 vibrations/sec.; distance apart of vibrators, 11.0 cm.; tension on elastic, 100 gm.

consisting of a mass and two lengths of string on either side equal to the semi-distance of separation of the masses. This frequency can be determined without difficulty and a comparison can be made with the frequencies the system will pass. An actual case is shown in figure 5.

Again, the lower limit should be the frequency of a single vibrator. This also is shown in figure 5.

In the range between, it is possible so to adjust the frequency of vibration that the half wave-length associated with it corresponds either with the length of the string or with some submultiple of this. In that case a system of stationary waves is formed, and there is no difficulty in obtaining several loops. By measuring these, and by measuring at the same time the speed of the motor, sufficient observations can be obtained to draw a graph relating wave-length and frequency. Such an experimental relationship is shown in figure 5, the observation being marked with circles.

It will be noticed that the data provide us with the means of calculating a relationship between wave-length and frequency from the formula

$$n = \frac{i}{2\pi} \sqrt{\left(\frac{4T}{ma} \sin^2 \frac{\pi a}{\lambda} + \frac{k^2}{m}\right)}.$$

The calculated values are marked with crosses.

Considering the various mechanical imperfections of the apparatus, the general agreement is satisfactory.

Since wave-velocity is given by the product of wave-length and frequency, it is easy to find this quantity from the graph. The wide range experimentally realizable is worth noting. Thus with a half wave-length equal to the length of the apparatus, the wave-velocity is 1080 cm./sec., whereas with a half wave-length equal to 16.3 cm. it is only 265 cm./sec.

§ 5. ANALOGOUS ACOUSTIC AND ELECTRICAL PHENOMENA

The most obvious analogy of the apparatus is to the acoustic and electrical filter circuits now well known*. In the electrical case the analogy is fairly complete, and the band-pass limits may be written down straight away. They are in fact the frequencies of the vibrator and the complete element. In the acoustic case, as Stewart found†, the inertia and elasticity factors are not so well located. Nevertheless the general analogy to the mechanical example remains, and only a band of frequencies is passed.

If (1) is reduced to differential form by making a very small, we have

$$m \frac{d^2 y}{dt^2} = T \frac{d^2 y}{dx^2} - k^2 y \quad \dots\dots(7);$$

m now refers to the mass per unit length, and k^2 to the force exerted by the springs per unit length per unit displacement.

This equation is now identical in form with that used by Sir J. J. Thomson to explain the properties of the Heaviside layer and the electrodeless discharge‡. It will be noticed that whereas the lower limit of transmission can be written $k/2\pi \sqrt{m}$, the upper limit has risen to an infinite value.

* Wood, *Sound*, p. 460 (1930).

† *Phys. Rev.* 25, 90 (1925).

‡ *Proc. Phys. Soc.* 40, 82 (1928).

We have therefore a high-pass filter. Waves below a certain frequency cannot penetrate such a medium, and, if incident upon it, are reflected back in the way now made well known by the extensive work of Appleton and others.

In the case of the electrodeless discharge, when the ionization is strong the frequency of the alternating currents is below the pass frequency, and the discharge consists of a ring close to the glass. The ring is very intense near the glass but fades away rapidly as we move inwards. In the case of the model, this is analogous to the way in which a vibration below the critical frequency fades away as we pass from mass to mass.

The model thus supplies a helpful analogy to a number of physical phenomena.

DISCUSSION

Dr W. G. BICKLEY. My attention was first drawn to the possibilities of mechanical models* of wave-filters by Crandall's* detailed examination of a set of equidistant heavy beads on a stretched string. This model, as he shows, would behave as a low-pass filter. A point which writers on electrical filter circuits do not mention is that the cut-off frequency is the frequency of a normal mode for the infinite system, in which neighbouring elements execute similar oscillations. A mechanical system with two such normal modes might be expected to behave as a band-pass filter. I conceived a model in which a number of equal heavy bars were joined together and were supported by equal springs at the joints; on paper, this shows the same properties as Dr West's model. It also has one interesting feature, that by increasing the radius of gyration of an element the cut-off frequencies can be made equal, so that all frequencies are stopped.

Mr W. F. FLOYD. It is evident, from the nature of the problem, that the most general solution is

$$y_s = Ye^{-K_1 s a} \cos (pt - \phi s) \quad \dots\dots(4a),$$

where ϕ is the phase displacement per section of the filter. On substitution in (1) in the paper, (4a) gives

$$\cos \phi \cosh K_1 a = 1 + ak^2/2T - 4am\pi^2 n^2/2T \quad \dots\dots(5a).$$

The above equations, (4a) and (5a), are analogous to (4) and (5) in the paper, but, since $+\infty \geq \cos \phi \cosh K_1 a \geq -\infty$, equation (5a) is valid for all values of n , whereas equation (5) is valid only when $k \geq 2\pi n\sqrt{m} \geq 0$. Free wave-transmission occurs when $K_1 = 0$; and at any instant it is evident that $\phi\lambda = 2\pi a$. Hence

$$n = \frac{1}{2\pi} \sqrt{\left(\frac{4T}{ma} \sin^2 \frac{\pi a}{\lambda} + \frac{k^2}{m}\right)},$$

and $\sqrt{\left(\frac{4T}{ma} + \frac{k^2}{m}\right)} > 2\pi n > \sqrt{\frac{k^2}{m}}$, as in the paper.

When $2\pi n < \sqrt{\frac{k^2}{m}}$, $\cos \phi$ must be positive; when $2\pi n > \sqrt{\left(\frac{4T}{ma} + \frac{k^2}{m}\right)}$, $\cos \phi$

* *Vibrating Systems and Sound* (Macmillan, 1927).

must be negative; when $2\pi n$ lies between these values, $\cos \phi$ may have any value from +1 to -1.

In particular, at the critical value, when $\phi = 0$, and $2\pi n = \sqrt{(2T/ma + k^2/m)}$, the whole system moves without phase-difference between its elements.

It must be emphasized that so far no account has been taken of reflection from the fixed end of the system. For this a term $Y_1 e^{-K_1 s} \cos(pt + \phi s + \theta)$ must be added to y_s in equation (4a). This added term is only important when $K_1 = 0$ and when $K_1 \rightarrow 0$. In the former case, $Y_1 = Y$ but the analysis becomes heavy.

In the electrical transmission-line analogue, the critical value, $\phi = 0$, corresponds to the case of optimum operation of the line, when no standing waves are present—i.e. there is a maximum transference of power over the line. Since a transmission line should never be operated so that wave-reflection occurs, the analysis for this case need not be considered. The model cannot illustrate the case of maximum power-transmission unless the remote end of the system be arranged to dissipate power into a characteristic load. For the range

$$\sqrt{\left(\frac{4T}{ma} + \frac{k^2}{m}\right)} > 2\pi n > \sqrt{\frac{k^2}{m}},$$

the model appears to be an exact analogue of a Lecher-wire system, but the reflection term should be added to (4a).

In the case of the electrical band-pass-filter analogue the band-width is generally small in comparison with the median frequency. On this assumption, the band-width is $2T/ak\sqrt{m}$ in angular frequency measure; the condition $\cos \phi = 0$ gives the median frequency.

Mr T. B. VINYCOMB. Dr West's model shows the characteristics of a band-pass filter very clearly. Historically, the same type of wave model was exhibited to the British Association in 1877 at Plymouth. Instead of a spring suspension for the masses, strings were used, so that they formed a series of connected pendulums. The natural periods were much longer than in Dr West's model as the object was to demonstrate group velocity. According to the account in *Nature* this phenomenon was very clearly shown. No mention was made of the peculiarities of the propagation at high or low frequencies.

The solutions for the different bands can be obtained very simply as follows:

Put $4T/m = \omega_2^2$ and $k^2/m = \omega_1^2$; then when a motion with time factor $e^{i\omega t}$ is being performed let there be a phase-difference ϕ between successive masses, so that

$$y_s = Ae^{i(\omega s - n\phi)}.$$

Then we get from equation (1)

$$-\omega^2 = \frac{\omega_2^2}{2} \left(\frac{e^{i\phi} + e^{-i\phi}}{2} - 1 \right) - \omega_1^2;$$

that is

$$\frac{1}{2}\omega_2^2 (\cos \phi - 1) = \omega_1^2 - \omega^2,$$

or

$$\sin \frac{1}{2}\phi = \sqrt{(\omega^2 - \omega_1^2)/\omega_2^2}.$$

This can be satisfied by real values of ϕ in the region

$$\omega_1 < \omega < \sqrt{(\omega_1^2 + \omega_2^2)} \text{ only.}$$

Write

$$\phi = \alpha + j\beta,$$

and we get

$$\sin \frac{1}{2}\alpha \cosh \frac{1}{2}\beta + j \cos \frac{1}{2}\alpha \sinh \frac{1}{2}\beta = \sqrt{(\omega^2 - \omega_1^2)/\omega_2}.$$

(i) If $\omega < \omega_1$,

$$\cos \frac{1}{2}\alpha \sinh \frac{1}{2}\beta = \sqrt{(\omega_1^2 - \omega^2)/\omega_2},$$

$$\sin \frac{1}{2}\alpha \cosh \frac{1}{2}\beta = 0.$$

Hence $\alpha = 0$, so that all the masses move in phase, and

$$\sinh \frac{1}{2}\beta = \sqrt{(\omega_1^2 - \omega^2)/\omega_2},$$

where $e^{-\beta}$ is the ratio of successive amplitudes. β decreases from ω_1/ω_2 to zero as ω increases from 0 to ω_1 .

(ii) $\omega_1 < \omega < \sqrt{(\omega_1^2 + \omega_2^2)}$,

$$\cos \frac{1}{2}\alpha \sinh \frac{1}{2}\beta = 0,$$

$$\sin \frac{1}{2}\alpha \cosh \frac{1}{2}\beta = \sqrt{(\omega^2 - \omega_1^2)/\omega_2}.$$

Thus $\beta = 0$; there is no attenuation but normal wave propagation. α ranges from 0 to π . The wave velocity is equal to $\omega d/\alpha$ and the group velocity is $d \cdot d\omega/d\alpha$ if d is the distance between the suspended masses.

(iii) $\omega > \sqrt{(\omega_1^2 + \omega_2^2)}/\omega_2$,

$$\sin \frac{1}{2}\alpha \cosh \frac{1}{2}\beta = \sqrt{(\omega_2^2 - \omega_1^2)/\omega_2} > 1,$$

$$\cos \frac{1}{2}\alpha \sinh \frac{1}{2}\beta = 0.$$

Here α remains equal to π , and successive masses move in opposite phases. β increases from 0 without limit as ω increases. This is the ordinary solution of a band-pass filter. In using any analogy between a mechanical or acoustic filter and an electrical filter care must be taken in identifying corresponding parts. For instance, in this model the elastic string connecting the masses in series is the analogue of capacitances shunting the line in the electrical case, and the spring strips which in the model appear in shunt, as it were, correspond to capacitances in series in the electrical line. It is best to work out each case separately, and compare the equations obtained in order to find the corresponding parts. The limiting frequencies are always found to be natural frequencies of the structure. Dr West's discussion of the motions of the model brings this out very clearly.

Dr L. E. C. HUGHES. In an electrical filter, the transmission engineer endeavours to arrange the elements so that there is no reflection of wave-energy in the pass band of the filter. For a complete representation of an electrical filter it is therefore necessary to use a termination which has the correct impedance over the pass range. In electrical filters this is possible in most practical cases, but would appear to be difficult in a mechanical model, although the cut-off frequencies can be clearly demonstrated. If in a T section of an electrical filter the total series impedance is Z_1 and the shunt impedance is Z_2 , the cut-off frequencies are given when $0 > Z_1/4Z_2 > -1$. Within this band there is maximum transmission, while outside

there is attenuation. To find the cut-off frequencies it is only necessary to insert ω in the above expressions for the impedances and solve for ω .

Capt. C. W. HUME. Mechanical wave-filters have been the subject of a number of inventions; the following British patent specifications may be of interest: 268,054; 258,395; 248,900; 243,321; and 221,792. Since it is a common practice to use only a small number of sections, the effect of terminal impedance is all-important. Within the transmission band the characteristic impedance is theoretically a pure resistance; could not the author illustrate this aspect of the problem by fastening the end *B* of his elastic to some sort of dash-pot having a minimum of inertia and resilience? At present his terminal impedance is infinite.

AUTHOR'S reply. I have followed up the suggestion made by Capt. Hume that the impedance of the terminal end of the model should be reduced, and, accordingly, light aluminium vanes have been attached to the end loads. By this method considerable air-damping is obtained and the model demonstrates, of course, that power is transmitted, but so far I have not been able to give any very striking demonstration of the variation of power transmission with frequency.

I agree with Dr Bickley that insufficient attention is given to the relation of cut-off frequencies to the free periods of the vibrating elements. In simple electrical filters these frequencies can be written down from direct analogy with the present model.

Mr Floyd's treatment of the equations is mathematically more comprehensive than my own, but the physical distinctness of the three cases makes me still prefer three direct solutions.

Mr Vinycomb's elegant use of imaginary quantities brings out well the continuity of algebraic form. The model he mentions would not appear to be well adapted for showing band-pass properties, but I have succeeded in modifying the model that he himself invented for this purpose.

THE MEASUREMENT OF IMPACT STRESSES IN CONCRETE

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ABSTRACT. A quartz piezo-electric gauge, used with a cathode-ray oscillograph for recording, to measure impact stresses in concrete has been developed. It is being employed to study the stresses in driven reinforced-concrete piles. Records illustrating the character of these stresses are given.

§ 1. INTRODUCTION

THE piezo-electric response of a quartz crystal to applied loads is practically instantaneous and a gauge making use of this property, with a suitable oscillograph for recording, forms the most accurate instrument yet available for studying impulsive or rapidly fluctuating pressures. The method has recently been applied to a number of problems. Gas pressures in the breech of a gun during the explosion of a charge have been measured by Webster⁽¹⁾; lathe cutting pressures, the starting torque of an electric motor, and impact stresses in a steel wire by Kluge and Linckh⁽²⁾; Grebel⁽³⁾ has described its use for recording the pressures in internal-combustion motors; Gechter and Laird⁽⁴⁾ have used apparatus similar to that of Kluge and Linckh in an investigation of the three components of tool pressure in a lathe.

The present paper is concerned with a further application—the investigation of impact stresses in concrete—and describes apparatus developed for the investigation of stresses occurring in reinforced concrete piles during driving. The work is being carried out at the Building Research Station in co-operation with the Federation of Civil Engineering Contractors.

§ 2. PRINCIPLES OF THE METHOD

The method is based on the fact that a hemihedric crystal with inclined faces, such as quartz, when compressed or elongated along one of the hemihedral axes, develops, at particular regions of the crystal, electric charges which are proportional to the applied force. The crystals forming the sensitive elements of gauges are cut from the natural material in the direction shown in figure 1 (*a*), that is, with a pair of faces perpendicular to the electric axis. Two ways of using the crystals piezo-electrically, which differ in the direction of application of the pressure, have been employed in previous researches, and the shape of the finished piece depends on which of these is used. In the first, figure 1 (*b*), in which the pressure is applied

along the electric axis, the quartz is generally cut in the form of a circular plate whose flat faces carry electrodes and are perpendicular to that axis. Two crystals are usually placed back to back so that the two outer electrodes are of the same polarity and are joined together and earthed. The middle electrode of opposite polarity is insulated by the quartz. In the second method it is most convenient to use a cube or long rectangular prism whose faces lie perpendicular to the electric, optic, and third or neutral axis. The pressure is applied along the third axis so that the electrodes, again on the faces perpendicular to the electric axis, are not subjected to compression, and for this reason the second method is adopted in the present research. The crystal, cut as in figure 1 (c), is mounted in a small water-tight chamber, described later in detail, which is cast in the concrete pile. Leads are brought out to a standard condenser across which, when the pile is stressed, a voltage is set up.

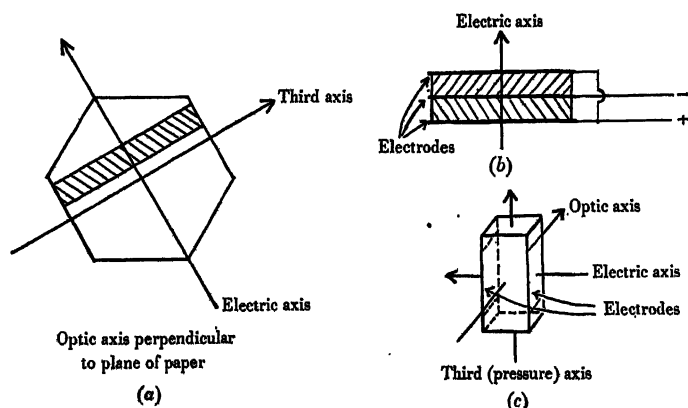


Figure 1. Position of axes in cut quartz crystals.

The two other main parts of the apparatus are the amplifier and the cathode-ray oscillograph. The amplifier is an important, and with commercial oscillographs an essential, component. Besides the requisite magnification of the voltage across the standard condenser, it provides, by the use of a special input valve, the very high resistance load across the quartz, which is necessary to reduce leakage to a negligible amount. This is particularly important for calibration, which is done by static loading. The input valve is, in the amplifier here described, an electrometer triode, but the double-grid valve has been used with equal success by Kluge and Linckh and other workers. The development of such valves of extremely high grid-filament resistance has rendered possible the use of the piezo-electric method with commercial cathode-ray oscillographs and with mechanical oscillographs of the Duddell type.

The cathode-ray oscillograph is unequalled for the conversion of transient electrical impulses into optical deflections. Its characteristics allow full advantage to be taken of the faithfulness of response of the crystal to pressure changes, and modern commercial examples have the additional merits of ease and dependability of working. Figure 2 is a theoretical diagram of the gauge, amplifier and oscillograph with auxiliary apparatus.

§3. EXPERIMENTAL

The gauge. Constructional details are given in figure 3. The quartz crystal 1 is a rectangular prism $\frac{3}{4} \times \frac{1}{4} \times \frac{1}{4}$ in.³ cut as in figure 1 (c) so that one pair of faces is perpendicular to the electric axis, and a second pair to the optic axis. Those perpendicular to the electric axis carry the electrodes 2 of electrolytically deposited copper. The electrodes cover about three-quarters of each face, leaving at each end a short length of quartz for insulation.

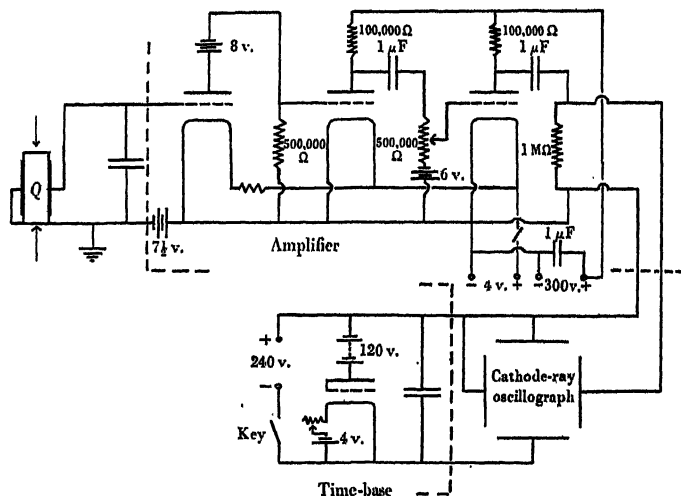


Figure 2. Electrical connections.

The prism is held between steel plates 3 to which the thrust is applied through steel balls. At one end a stiff spring 4 is inserted between ball and plate to reduce the stress in the quartz.

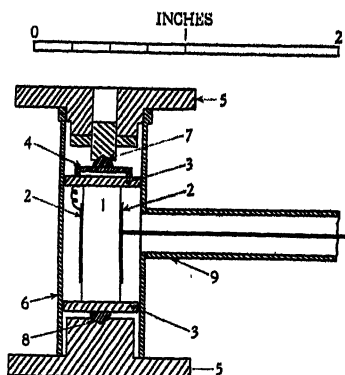


Figure 3. Section of a gauge.

Two heavy circular steel end-plates with projecting flanges 5, connected by a thin brass cylinder 6, form a water-tight chamber enclosing the crystal. The latter is held between conical seatings 7 and 8, of which one is adjustable. A highly insulated lead is brought out from one electrode through the brass tube 9, while the other electrode is earthed to the case.

When the apparatus is assembled a permanent load is put on the crystal by screwing up the adjustable seating 7. The gauge then responds to tension, which its flanged shape, affording a key for the concrete, enables it to follow.

The amplifier. The essential feature of an amplifier for piezo-electric work is that the grid-filament resistance of the input stage shall be very high. This is ensured by the use of the General Electric Company's electrometer valve which has a grid-filament resistance of $10^{15} \Omega$. The complete amplifier, figure 2, consists of this valve followed by two L.S. 5. B. valves. The first and second stages are direct coupled. Resistance-capacity coupling links the second to the third valve, and the third to the vertical deflecting plates of the oscillograph. The overall amplification is 48·7, to which the first stage contributes a factor of about unity. Provision is made for varying the amplification by means of a calibrated grid potentiometer in the second stage, but this control is rarely used as it is generally more convenient to vary sensitivity by altering the parallel capacity across the gauge. The amplifier is housed in a shielded box, into which the lead to the input grid is carried by a heavy ebonite tube.

The condenser in parallel with the gauge has a value of $0\cdot001 \mu\text{F.}$ to $0\cdot003 \mu\text{F.}$, large enough for small changes in capacity of leads to be negligible.

For the static calibration of gauges, the amplifier is arranged to have an input resistance of not less than $10^{12} \Omega$., but for working purposes this is with advantage reduced to about $10^9 \Omega$., to allow charges induced on the grid by external disturbances to leak away in a reasonable time.

Recording-equipment. The oscillograph is manufactured by Messrs Cossor, Ltd., and is operated for photography at an anode potential of 1500 V. provided by a high tension unit from the a.-c. mains.

Records are taken with a stationary plate camera and a single-traverse time base. In this method⁽⁵⁾, which is suitable for the registration of phenomena of short duration, a voltage varying linearly with time is impressed on the horizontal plates of the oscillograph at the appropriate moment so as to cause the spot on the fluorescent screen to move horizontally across, while the voltage from the gauge is simultaneously impressed on the vertical deflecting plates. The (stress, time) pattern thus delineated on the screen is photographed with a stationary camera.

The time-base circuit, figure 2, is made up of a condenser charged by a battery and discharged through a saturated diode by the opening of a switch at the correct moment. The speed of the spot across the screen is controllable between 1 and 10 m./sec. by variation of the condenser capacity and the saturation current of the valve.

A quarter-plate camera with a Ross Xpres f. 1·9 lens of 3 in. focal length is fixed relative to the oscillograph and gives a slightly reduced picture of the screen. A lens cap, hand operated, serves as shutter.

A time scale of milliseconds is impressed on the same plate as the record by a second exposure. After a stress record has been made the oscillograph is switched over to a fixed frequency 1000-cycle oscillator and a photograph of the wave-form is taken with the same time-base speed as before.

§ 4. CALIBRATION

Two operations are required for calibration. The overall sensitivity of amplifier and oscillograph is determined in the first and expressed as photographic deflection in mm. per grid volt of the amplifier. This is found by applying known voltages suddenly to the grid of the input valve and photographing the oscillograph deflections. Two switches are inter-connected so that the time base is released and the calibrating voltage is applied immediately afterwards. This gives a record of stepped type well adapted for measurement. The overall calibration was checked frequently during the taking of records in order that allowance might be made for any alteration in the sensitivity. No appreciable differences were observed.

The second part of the calibration is the determination of the sensitivity of the gauge in concrete in terms of charge developed per unit strain. The gauge is cast at the mid-point of the axis of a block of concrete $16 \times 4 \times 4$ in.³ of the same constitution as the concrete in which stresses are to be measured, and subjected to the

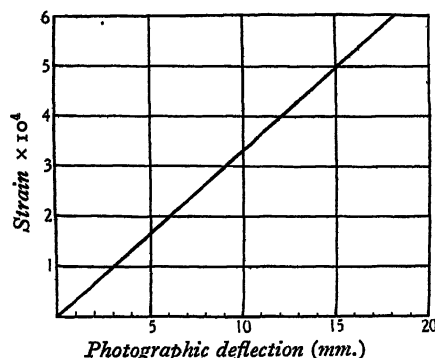


Figure 4. Sensitivity of gauge J. with 0.002 μ F. condenser.

same treatment. The block is stressed up to 3000 lb./in.² in a testing machine, measurements of strain being taken with a two-inch roller extensometer with telescope and scale, over the two-inch central portion in which the gauge is situated. The charge developed by the gauge produces across a standard condenser a voltage which is measured with a direct-coupled amplifier, constructed by removing the third valve of the amplifier and inserting a galvanometer with balancing circuit in the plate circuit of the second valve. Each time that it was used this instrument was calibrated by the application of known voltages from a potentiometer.

The procedure was to measure strain across the section containing the gauge, and charge developed for a number of increments of stress. A curve was then drawn between charge, or voltage across a standard condenser, and strain. Both parts of the calibration provide linear relationships, so that the resulting graph of photographic deflection against strain is a straight line, figure 4. The sensitivity in tension is obtained by extrapolation. In the interpretation of records, strains are converted to stresses by multiplying by the statically determined Young's modulus. This procedure is discussed below.

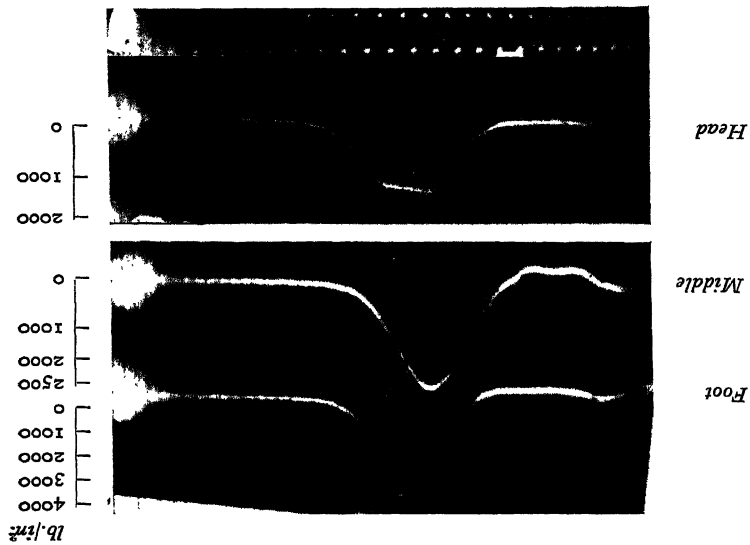


Figure 5. 12-inch drop of 1000-lb. hammer. Foot of pile bolted down to rigid base. Head buffered with 1 inch of felt.

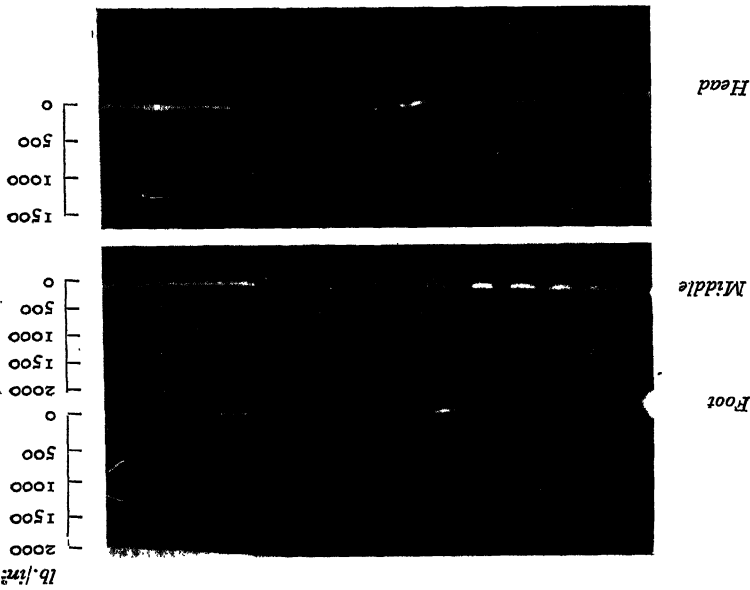


Figure 6. 6-inch drop of 1000-lb. hammer. Foot of pile on $\frac{1}{2}$ -inch felt on rigid base. Head buffered— $\frac{1}{2}$ -inch felt beneath 3-cwt. helmet above which is a 12-inch elm dolly.

The accuracy of calibration in terms of strain is estimated to be subject to an error of ± 5 per cent. It is, however, possible to be in error by approximately ± 10 per cent in the stresses calculated from these strains. The chief cause is probably the difficulty of assigning the correct modulus to the block of concrete in which the gauge is cast. Large differences of Young's modulus are frequently observed between blocks of concrete of the same mix and curing-treatment, and the only way of avoiding error is to measure the modulus directly over each gauge, which in the majority of cases is impracticable. There is also no direct evidence that the (stress, strain) relationship of concrete is the same in impact as that determined statically.

Two checks on the accuracy of stress-measurement may be made from the records. The first is the calculation of Young's modulus for a pile from the observed frequency of longitudinal vibration, and the second is the comparison of two calculations of the momentum of the hammer, the one made from the stress record at the head of the pile and the other from the measured heights of drop and rebound. These give the figure of ± 10 per cent and are further referred to in the next section.

§ 5. WORKING DETAILS. IMPACT STRESSES IN DRIVEN REINFORCED-CONCRETE PILES

Measurements of stress have been made in reinforced-concrete piles measuring 15 ft. \times 7 in. \times 7 in., in which gauges were cast 4 in. from each end and at the mid-point of the length. The piles were driven with a drop hammer falling freely.

The recording apparatus was set up in a hut measuring 10 ft. \times 8 ft. close to the pile-driving frame. It was found that with the comparatively large parallel capacity used, generally 0.002 μ F., unshielded leads of bare copper wire on porcelain insulators were perfectly satisfactory except on very wet days. A separate insulated lead from each gauge was brought to a change-over switch in the hut by which each could be connected in turn to the amplifier. The chambers enclosing the crystals were connected to a common earth lead and to the amplifier.

The switch in the time-base circuit was set up on the pile-driving frame on an adjustable mount and so arranged that the hammer in its descent tripped it at the correct instant for recording purposes.

A traverse speed of about 3.5 m./sec. across the screen was normally used. Since records from the three gauges in the pile could not be made simultaneously, a complete series for any one condition was obtained in three or, if a check was necessary, four consecutive blows.

Records for two different conditions of driving are reproduced in figures 5 and 6. Figure 5 is of the simplest type obtained. The pile is bolted down against a rigid concrete foundation and on the head a buffer, consisting of 1 in. of felt, is placed. The hammer weighs 1000 lb. and the drop is 12 in. Under these conditions the curves at head, middle and foot are smooth, and the maximum compression at the foot is approximately twice that at the head. After the hammer has rebounded, tensions are set up at the middle, and to a smaller extent at the foot. Figure 6 represents easier driving, the foot of the pile resting on a felt packing on the rigid base. The buffer is the arrangement used in practice, a heavy iron helmet in the top

of which is fitted an elm block or dolly, while beneath it a felt packing protects the pile-head. Mathematical investigation⁽⁶⁾ leads us to expect that the pile will behave as a long thin rod, and that stresses in the pile will, at a given instant, vary along its length, and at any one point will fluctuate in a periodic manner. Quantitative agreement with theory has not yet been reached, but the records in figure 6 clearly illustrate the wave character of the stresses. The frequency of longitudinal vibration is well brought out in the record at the centre, where slight tensions are set up by the residual vibration. The apparent tensions at head and foot are due to electrical leakage. After the hammer has rebounded, the ends of the pile are antinodes and the middle a node. The frequency of vibration is 455 c./sec., whence Young's modulus for the pile is 5.7×10^6 lb./in.² The value calculated from the moduli of concrete and steel is 5.35×10^6 lb./in.² The (stress, strain) relationship from the impact record therefore agrees with that determined statically within 7 per cent.

This is the first check on the accuracy of measurement of stress, mentioned in the preceding section. The second is provided by calculating the momentum change of the hammer.

At the head of the pile the force exerted downwards over the cross-section is, at any instant, equal and opposite to that decelerating the hammer, provided that the effect of the buffer can be neglected. Then it is easily shown that the total momentum change

$$M(V - v) = A \int_0^T P \cdot dt,$$

where M is the mass of the hammer, V and v its velocities immediately before and after striking, A the area of the pile-head, P the stress at the head of the pile, and T the duration of the blow.

The integral is proportional to the area under the (stress, time) curve of the gauge at the head, and the left-hand term is immediately determined from the heights of drop and rebound. Calculations thus made agree within 10 per cent.

§ 6. ACKNOWLEDGMENTS

The author wishes to acknowledge his indebtedness to Mr Wilsdon and Mr A. F. Dufton under whose supervision the work has proceeded; to Dr W. Glanville for advice and criticism, and to Mr C. T. Webster for general assistance. He desires also to express his grateful thanks to Mr J. F. Herd of the Radio Research Station for his generous assistance in the design and construction of the amplifier, time base, and oscillator.

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DISCUSSION

Mr H. W. HEATH. The paper calls for criticism of the mechanical principle involved, namely, embedding in a concrete pile a foreign body (the gauge), obtaining data from the deformation of that body while so embedded, and interpreting the result as stress in the concrete.

The results would be completely misleading unless the Young's modulus for the complete gauge is the same as that of the concrete. The method of calibrating the gauge is subject to the same criticism.

The state of stress inside the test piece can be followed by considering a compound bar made by welding together, side by side, a copper and a steel bar, and applying an end load. The strain would be the same for both bars, but the stresses are in the proportion of the respective moduli; and the part of the load taken by either bar is the product of the area of that bar and the stress in that bar, the sum of these two products being equal to the total load.

Precisely the same conditions apply to the calibration of the gauge when embedded in the test block to determine the relation between strain and pressure (or charge). At the cross-section containing the top of the gauge the stress is not uniform, and the charge developed depends on the two moduli (concrete and gauge separately), and on the relative areas of test piece section and top plate of gauge. Moreover, the straight-line law obtained from the test block is not applicable to the reinforced pile, since the area of the pile is 49 in², and about 2 in² of this is steel equivalent to, say, 30 in² of concrete, so that the steel rods take nearly half the load.

The essential information required for the test is the Young's modulus for the complete gauge, as shown in figure 3, when it is not embedded in concrete. A relation can then be deduced between the pressure on the end plates when embedded and the strain on the face of the test piece. This relation must then be modified because of the difference in area between pile and test piece, and further modified to allow for the share of the reinforcement in the load, and for the suddenness of the load applied to the pile as distinguished from the load applied statically to the test piece.

Bearing in mind that stresses in a cross-section can vary enormously at two points separated by only a centimetre, it would be miraculous if the stresses recorded were anywhere near those actually developed in the pile.

The only reliable information emerging from the test is the frequency of the longitudinal oscillations, and hence the Young's modulus for the whole pile.

AUTHOR'S reply. Mr Heath has lost sight of the fact that the charge developed depends directly upon the stress in the quartz but only indirectly upon the pressure exerted upon the end plates when the gauge is in position. The strain suffered by the gauge is likely to be the same as that of the concrete in which it is embedded. Assuming this, it is readily seen that since the charge developed is proportional to the stress in the quartz, it will be proportional to the relative movement of the end plates and so to the strain in the concrete. We therefore measure strain in the

concrete, from which stress is derived in the usual manner. It is therefore not at all necessary for the interpretation of results to know anything of the constants of the gauge. An estimate of the stiffness is useful however for design purposes in order to ensure that the stiffness shall be approximately equal to that of the concrete.

Finally, we are at present interested only in the average stress over the cross-section, and not in the variation which must be present in a non-homogeneous material such as concrete. That this is being measured with reasonable accuracy is confirmed by the agreement now being obtained between the measured stresses and those calculated from theory.

ADDENDUM

“THE MEASUREMENT OF IMPACT STRESSES IN CONCRETE”

By G. GRIME, M.Sc., Building Research Station

The following part of the author's reply to the discussion was omitted in error :

The calculation of load taken by the steel is inapplicable to the piles under discussion. These had either 0.5 per cent or 2.5 per cent longitudinal reinforcement, which, with concrete having a Young's modulus of $5 \cdot 10^6$ lb./in.², would take 3 per cent and 13 per cent respectively of the load.

AN AUTOMATIC PHOTO-ELECTRIC PHOTOMETER

By ERIC B. MOSS, B.Sc. (Lond.)

Received October 14, 1933. Read December 1, 1933, with demonstration.

ABSTRACT. A precision photo-electric photometer based on principles capable of wide application and operated from a.c. mains is described. It is a flicker instrument but the simple shutter is on the spindle of a synchronous motor driven from the same supply as an a.c. valve bridge. This is connected to an emission type photo-cell, and gives a directional output which automatically moves the neutral density wedge to the position of balance which is shown by a pointer. The wedge position is controlled electrically, being mounted on a galvanometer movement devoid of mechanical control.

A description of a densitometer for liquids is given.

§ 1. INTRODUCTION

NUMEROUS photo-electric photometers have been described whose general purpose is to compare two intensities of either transmitted or reflected light*. These instruments are as varied in design as in purpose, and usually they have been intended for laboratory use, so that to make one instrument suitable for general use it is necessary to design yet another apparatus.

Briefly, the object of the design is a reliable instrument which can be used by routine operators, or experimenters skilled only in their particular branch of science. In their hands it must yield, for subsequent interpretation, readings of optical density or reflective power with sufficient accuracy and in a minimum of time. The demand for reliability makes it necessary that the instrument shall work from alternating-current mains.

The alternative-path or flicker principle is used because it eliminates the effect of changes in the sensitivity of the photo-cell, or in the brilliance of the light source, but the optical system is so arranged as to overcome the difficulty sometimes experienced in adjusting the shutter so that one beam may be opened and the other closed at exactly the same rate. The design of the shutter also ensures that any flicker shall be of sinusoidal wave-form and thus be capable of being amplified efficiently by means of a simple valve amplifier. The valve amplifier gives a directional d.-c. output when the intensities are unequal. This is secured without the use of a commutator, since it is found in practice that a small commutator used in conjunction with a galvanometer can give trouble. Inequalities of the beams are balanced by means of a neutral optical wedge. This is moved automatically without relays, by the output from the amplifier, and its position is shown by a pointer on a scale. This feature has points of similarity with one described by A. C. Hardy†, but in the present instrument the end is achieved in a simpler manner.

* See the end of the paper.

† A. C. Hardy, *J. Opt. Soc. Amer.* 12, 96 (1924).

§ 2. THE OPTICAL SYSTEM

A diagrammatic arrangement suitable for measuring optical densities is illustrated in figure 1. It has two symmetrical halves whose axes have a common origin at the lamp filament and terminate on the cathode of the photo-cell. One axis is through the lenses A_1 , B_1 , C_1 , D_1 and prisms K_1 , L_1 , while the other passes through the components A_2 , B_2 , C_2 , D_2 and L_2 . The axes therefore intersect at O . An image of the lamp-filament is formed by lens A_1 on B_1 , and the latter is calculated to produce an image of A_1 at the intersection O . The field lens C_1 forms an image of the

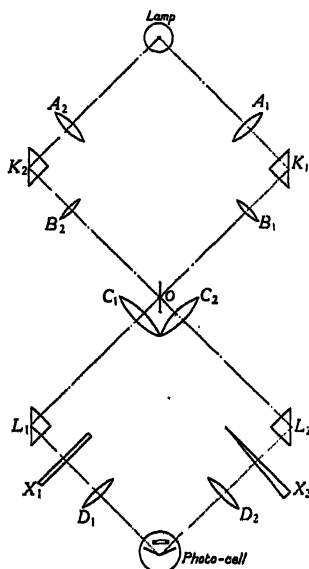


Figure 1.

filament at X_1 , at which point is placed the unknown density. Subsequently the diverging beam is concentrated by lens D_1 on to the photo-cell cathode. The other half of the optical system is identical except for the insertion of the adjustable balancing wedge at X_2 . Mounted at O , so as to be perpendicular to the plane containing the two optical axes, is an extension of an electric-motor spindle. This carries a thin disc slightly smaller in diameter than the image of A_1 or A_2 , so that as the spindle rotates first one and then the other beam is obstructed. The quantity of light in each path will vary harmonically with time at a frequency double that of the motor-speed, and one will lead the other by 180° . This angular displacement is dependent on the lay-out of the optical components. It can therefore be made with precision and is not liable to derangement. Clearly, then, any inequality in the two beams will give rise to a sinusoidal light-fluctuation whose phase will depend on which beam is the brighter.

It will be seen later that only that harmonic portion of the photo-electric current

which is synchronous with the shutter rotation affects the amplifier. Therefore it is essential that this shutter shall rotate in a uniform field. It does not matter if the field is considerably larger than the circle of the disc, but the need for maximum sensitivity makes a large margin undesirable. In practice the diameter of the shutter is about 1 mm. less than that of the images of A_1 and A_2 .

With a little modification the system can be made suitable for comparing the reflective powers of matt materials such as paper, cloth and powders. The standard and sample may be placed side by side just in front of the position occupied by the photo-cell in figure 1. In this position one beam would fall on each, and the photo-cell would be placed on the centre line of the system but facing the specimens so as to receive an equal proportion of the light reflected from each. The efficiency of such a simple system could be increased, for example, by the interposition of a field lens between specimens and photo-cell.

§ 3. THE VALVE AMPLIFIER

A phase-sensitive detector is necessary to take advantage of the phase-change which results from inequality of the two light-intensities, and the valve bridge due to C. R. Cosens* has been chosen as being very suitable. By its use rectifiers and smoothing accessories are dispensed with and this saves considerable space.

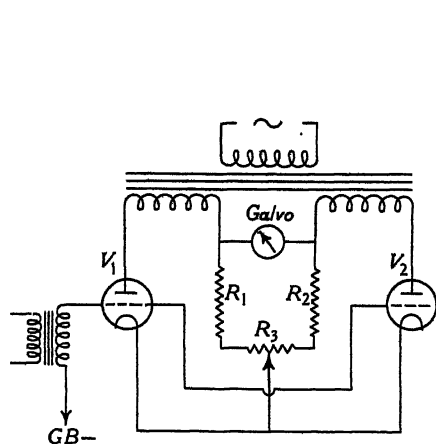


Figure 2a.

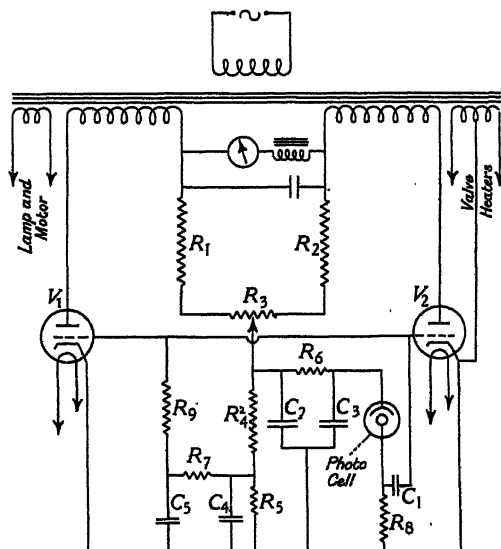


Figure 2b.

The simple circuit is shown in figure 2a. It consists of two valves V_1 and V_2 with their anodes connected to separate windings on the same transformer so that they are in anti-phase, the anode-cathode circuits being completed by the resistances R_1 , R_2 and a potentiometer R_3 . If the valves are matched and their grids

* British Patent Specification, No. 385,982.

tied together to the correct bias, then during one complete cycle each will pass the same current. This results in the mean current through R_1 being equal to that through R_2 . The galvanometer can be zeroized even if the valves are not perfectly matched, by adjusting the tapping on the potentiometer R_3 .

Suppose now that through the grid transformer a small alternating e.m.f. is applied to the valve grids in phase with the anode supply to V_1 . During one half-cycle the grids will be slightly more positive than the steady grid-bias when the anode of V_1 is positive, and more current will flow through V_1 and R_1 . During this half-cycle the anode V_2 is negative and no current passes through the valve. During the next half-cycle the grids are more negative and therefore less current will pass through V_2 and R_2 than passed through V_1 and R_1 in the previous half-cycle. The continuous effect is to impart a steady deflection to the galvanometer. Should the phase of the grids be reversed, then the galvanometer will be deflected in the opposite way because the mean current through R_2 will be greater than that through R_1 .

Certain modifications are necessary to the valve bridge so that it may be suitable for operation entirely from alternating supply. The complete circuit is shown in figure 2*b*. A smoothing circuit has been added to the galvanometer, and further additions are resistances R_4 and R_5 . The sum of these two is such that the total rectified current through the valves gives a potential-drop suitable for the operation of a photo-cell. The resistance R_5 is that for automatic grid-bias, and R_6 and R_7 are added in conjunction with a condenser for smoothing. The values of the resistances and capacitances used in the densitometer described later in this paper are as follows:

	Ω .		μF .	
R_1, R_2	3000	C_1	0.1	
R_3	400	C_2	2.0	(electrolytic)
R_4	20,000	C_3, C_5	0.5	
R_5	800	C_4	50.0	(electrolytic)
$M\Omega$.				
R_6, R_7	0.25			
R_8, R_9	2.0			

The transformer was wound to give 230 volts on the valve anodes. Valves of the Osram Catkin type were chosen partly on account of their small size. These have an impedance of 11,100 Ω . and a mutual conductance of 3.6 mA./V. The resistance of the moving coil of the wedge movement is 1000 Ω . and that of its choke 100 Ω .

Up to this point, by the galvanometer has been meant an ordinary instrument with a suspended or pivoted movement under a definite mechanical control. Hereafter this conception must be forgotten, as the movement used in the instrument is devoid of mechanical control and is held in its correct position electrically.

One requirement which this bridge satisfies is that it shall not be effected by even harmonics of the fundamental frequency, e.g. the frequency of the supply to the transformer. This is vital because the illumination from a gas-filled-lamp filament is modulated to a considerable depth at these multiple frequencies. The

second harmonic is predominant and it is essential to ensure that the voltage developed on the valve grids at this frequency shall not be sufficient to cause over-loading.

There may be conditions, as in spectrophotometry or in measurements with reflected light, when such intense illumination of the photo-cell may not be available. Under these circumstances the sensitivity can be increased by preceding the valve bridge with one stage of amplification. If this is done, however, it is more important than ever to ensure that over-loading of the bridge shall not be caused by the second harmonic.

An alternative to the use of this valve bridge would be to employ a straight amplifier with a dynamometer connected to the output and used as a detector. The fixed coils of the dynamometer would be fed from the supply, and the directional characteristic would be retained.

§ 4. THE MOTOR

The frequency co-ordination between the valve-bridge supply and the shutter-disc rotation is secured by the use of a synchronous motor connected to a winding on the same transformer. This motor is a four-pole machine and was specially designed for the instrument. The rotor turns at half the synchronous speed, but since one complete cycle of light-change takes place in half a turn the change is at the fundamental frequency. The motor is illustrated in figure 3.

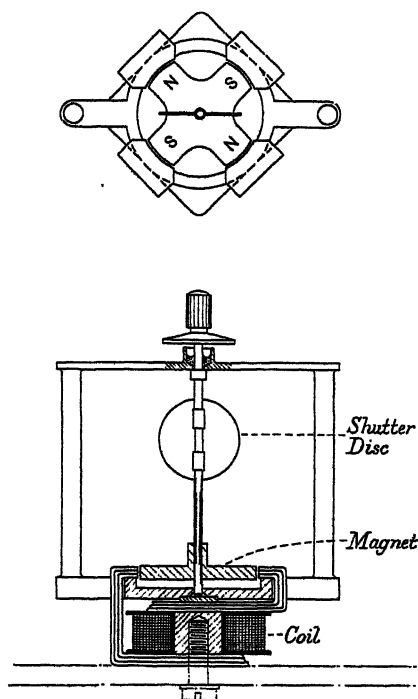


Figure 3.

It is further necessary that the alternating voltage which appears on the valve grids in the out-of-balance condition of the beams shall be in phase with the anode-voltage of the correct valve. If it is not so, clearly the sensitivity is reduced in the proportion of the cosine of the angle of error, provided that the latter is not greater than 90° . Should this be exceeded it means that the out-of-balance e.m.f. is coming into phase with the other valve supply, and this is equivalent to reversing the output of the bridge. The effect which this has will be mentioned later.

The phase is dependent on the position of the motor stator in relation to the optical work, and this is readily adjusted by rotation since the motor is held down by one central screw. At the base is the field coil which is wound for a 6-volt supply as it is connected in parallel with the lamp. Above this are the four poles, their magnetic path inside the coil being completed by a slotted mild-steel core. The poles are fastened to a brass disc which has a hardened steel bearing at its centre to support the vertical spindle on to which the cross-shaped permanent magnet is forced. Above it is the top bearing in a bridge piece, while higher up the shaft is the shutter disc and the starting head. This latter is used to start the motor by means of a sharp twist given with the finger and thumb. Synchronism is obtained on any commercial supply frequency, and such changes as are likely to occur when the instrument is in use are followed instantaneously and without hunting. On a 50-cycle supply the current consumption is 0.6 A.

§ 5. THE NEUTRAL-DENSITY WEDGE AND ITS ADJUSTMENT

For this instrument the wedge is prepared on celluloid and is approximately 10 mm. wide and 70 mm. long. The choice of density-range must depend on the purpose of the instrument. The wedge is bent to an arc and mounted upon the moving coil of an ordinary millivoltmeter assembly*; it is held in a very light bent channel of aluminium which is carried by two supporting arms from the central clip which unites the coil, counter-weights, and pointer to the top pivot. A lower pivot in the customary clip completes the assembly, which is mounted on jewels in the usual way. The wedge is concentric with the pivot axis, but considerably above the upper pivot so that the optical path is unobstructed. The pointer is opposite to the wedge but in a lower plane. Figure 4 shows the arrangement of the coil, pointer and magnet system relative to the curved wedge.

The circuit through the coil is completed by two ligaments of thin silver-gilt strip. These exert a negligible mechanical control, and when disconnected from the instrument the movement tends to stay wherever it is placed. It is connected electrically in the place of the galvanometer in figure 2*b*. Now it will be remembered that the polarity of the valve-bridge output depends on which beam is the brighter; consequently if the wedge is in one beam it will be possible so to connect the moving coil that the wedge will be moved in the direction requisite to restore a balance. It will only cease moving when this is attained; that is, when the current through the

* This assembly without the pointer is the standard arrangement for the projected-scale instrument of the Cambridge Instrument Co., Ltd., by whom it is patented (British Patent Specification, No. 380,654).

coil is zero. The pointer-reading is then a measure of the density which has been inserted to equalize the transmissions of the two paths, and this reading will have been given by a truly null method.

Should the coil be connected in the reverse direction a balance will not be reached. On the contrary it will move away from the balance point on whatever side it happens to be and its excursion will only be limited by the stops of the instrument. This behaviour is seen if the synchronous motor is started by turning in the wrong direction, or if the phase of the grid-voltage is reversed, as was discussed in the paragraph dealing with the motor.

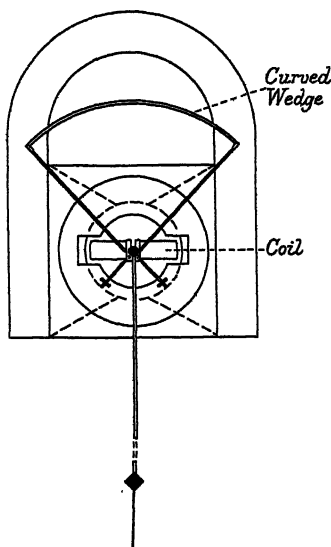


Figure 4.

§ 6. DENSITOMETER FOR LIQUIDS

An instrument incorporating the preceding features and designed to measure the optical densities of liquids will now be described. The ideal symmetrical optical arrangement of figure 1 is abandoned in favour of a more convenient layout, but the optical paths still form a pair of equal rectangles. The line joining K_2 and L_2 now forms the centre line of the instrument. The optical work is assembled on a stout plate which fits the case except in one corner where it is cut away to make room for the taller parts of the electrical equipment, all of which is carried on a separate sub-panel.

The scale is clear and its position makes it easy to read. Immediately below it is the milled edge of the rheostat adjustment for balancing the bridge, and the mains switch.

The instrument is used as follows. When current is first switched on the bridge will generally be found to be out of balance, but after ten minutes the valves should have reached a steady condition. Since there is no mechanical control on the

galvanometer, lack of balance of the bridge is shown by a steady drift of the pointer. The effect of an error is therefore cumulative, and adjustment can be made most precisely. This is done by moving the rheostat, which is that shown at R_3 , figure 2*b*. The motor can afterwards be started and when it has come into synchronism the pointer will move to its appropriate position, coming to rest in about three seconds. To re-check the bridge-balance at any time it is only necessary to stop the motor. It is found that after several hours' working without readjustment the balance of the bridge is not sufficiently far out to cause an error of more than 0.2 of a scale division. The scale is divided into 100 divisions.

The scale-readings represent uniform changes of an approximately neutral density, and usually an experimental calibration is made to determine the relationship between the scale-readings and the concentration of a precipitate or of a coloured ion in the liquid. This is done by noting the readings when the cell, containing in succession different known concentrations of solute, is placed in the instrument.

When measurements are being made on a coloured liquid the instrument reading is a measure of the liquid-transmission for a certain band of wave-lengths, in terms of the transmission of a neutral wedge for that band, emitted by the lamp, to which the photo-cell is sensitive; consequently the relationship will change with the colour temperature of the source. The instrument under discussion is intended to operate from supply mains, and therefore changes in colour temperature are unavoidable. To circumvent this source of error a colour-filter must be used in each beam, and this filter should pass the colour complementary to that transmitted by the liquid. Care must be taken not to reduce the illumination too much in this way, or the error which might exist owing to changes of lamp-temperature will be replaced by that resulting from loss of sensitivity. The inherent colour-sensitivity of the photo-cell may in some cases suffice, but in general the use of a filter is beneficial provided that the filter is correctly chosen.

In this particular instrument illumination is provided by a 6-volt 24-watt gas-filled car head-lamp bulb, and is sufficient to give a maximum out-of-balance potential on the grids of 16 volts r.m.s., and it is found that the output from the bridge is 0.8 milliampere for an input of 1 volt r.m.s., with a load resistance 1100 Ω . If T represents the transmission of the beams, T_0 can correspond to the maximum transmission. The sensitivity of the device will be represented by $\Delta T/T$. It is convenient to express T in terms of grid volts.

Then

$$T_0 = 16 \text{ V.},$$

and

$$\Delta T = 10^{-4}/0.8 \text{ V.},$$

therefore

$$\Delta T/T_0 = 8 \times 10^{-6},$$

and it follows that the sensitivity will be proportional to T . This theoretical sensitivity is never attained in practice, on account of the limitation imposed by fluctuations in the mains-voltage, but it is found that in spite of these it is possible at the maximum transmission to measure to 0.1 per cent, the possible error increasing to 1.0 per cent, at a transmission of 1 per cent, i.e. a density of 2.0.

It is worth noting perhaps that the voltage on the valve grids due to the second harmonic is 0.6 under conditions of maximum illumination.

§ 7. ACKNOWLEDGMENTS

I wish to record my gratitude to the directors of the Cambridge Instrument Co., Ltd., at whose suggestion this description has been published.

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The following is a list of some references to published descriptions of photometers. It does not pretend to be exhaustive.

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SOME MEASUREMENTS OF MAGNETIC SUSCEPTIBILITIES AT HIGH TEMPERATURES

BY R. A. FEREDAY, PH.D., F.INST.P., East London College

Received October 2, 1933. Read January 19, 1934.

ABSTRACT. Details are given of an electromagnet which has been specially built for carrying out measurements of small susceptibilities by a method, previously described by the author, in which specially designed pole-pieces are used. It is shown that the method is applicable whether the pole-pieces are or are not saturated. An apparatus for the determination of susceptibilities at high temperatures is described in detail. It is shown that the susceptibility of anhydrous nickel sulphate can be represented by an expression of the form $(\chi - a)(T - \theta) = C$, and that anhydrous nickel cyanide, although having an exceptionally small susceptibility (of the order 3×10^{-6}), behaves as a normal paramagnetic substance, following a Curie-Weiss law for variation of susceptibility with temperature.

§ 1. INTRODUCTORY

IN a series of earlier communications to these *Proceedings** an account has been given of the development of a new method for the determination of the susceptibilities of para- and dia-magnetic bodies at room temperatures. The method is of the non-uniform field type, in which the body under examination is suspended in a non-uniform magnetic field, the tractive force exerted upon it being measured by means of a torsion balance; and its peculiar feature is that, as a result of special design of the pole-pieces of the electromagnet producing the field, a large region exists over which the force exerted upon the body has a constant value. This overcomes the difficulty usually met with in methods based on the non-uniform-field principle, that the force exerted on the specimen varies very rapidly from point to point in the field, so that the body must be located with considerable accuracy—usually at a point of maximum force.

The only electromagnet available for the earlier work was of very unsatisfactory design, and was not capable of magnetizing the pole-pieces to saturation. A result of this was that difficulty was experienced in practice, owing to serious variations in H with variations in supply voltage; further, it was not certain that a similar field-distribution could be realized if the pole-pieces were saturated.

Through the interest of Prof. H. R. Robinson and the Metropolitan-Vickers Electrical Co., I have been able to obtain a new electromagnet designed specially for the purpose of continuing this investigation. This paper describes the instrument, and its application to an investigation of the effect of saturation of the pole-pieces on the field-distributions obtained. It was found that no essential change was

* *Proc. Phys. Soc.* 42, 251 (1930); 43, 383 (1931); 44, 274 (1932).

necessary in the principle of the new method for susceptibility-measurements when the new magnet was used, and the immunity from trouble due to voltage-fluctuations enabled measurements to be made with considerably greater ease than previously.

The apparatus was modified to allow measurements to be made at temperatures up to 450°C. , and an account of this new apparatus, with some results of high-temperature measurements, is included.

§ 2. THE ELECTROMAGNET

The main factors to be considered in designing the magnet were (1) ability to produce saturation of the pole-pieces when working at a gap of some 35 mm., and (2) effective cooling, since a rise in temperature would produce a change in permeability of the material of the pole-pieces, leading to changes in the magnitude and configuration of the field.

The design adopted is illustrated by figure 1. In order to allow a tapering section for the purpose of concentrating the reluctance at the gap, and at the same

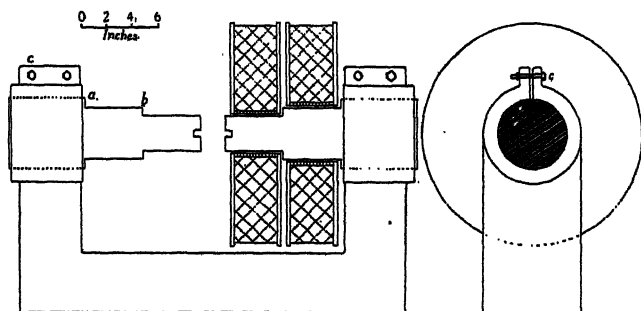


Figure 1. The electromagnet.

time to allow of free movement of the poles when the gap-width is being adjusted, the poles are stepped at *a* and *b*, and the winding on each is divided into two sections, so that the whole winding is contained on a total of four bobbins. The poles are turned to be a close sliding fit in the bored-out parts at the top of the yoke, and after adjustment of the gap-width they are locked in position by the bolts *c*. The use of this method of construction instead of the more usual screw adjustment, although it makes the initial adjustment of the gap more difficult, has the advantages of simplifying construction and maintaining better alignment of the two poles.

The yoke was cast from a pattern which was very kindly placed at my disposal by Dr J. D. Cockcroft.

The magnet is water-cooled, each of the four sections of the winding being carried by a hollow-walled bobbin which forms a complete water jacket round it. The cylindrical core of each bobbin is formed by a closely coiled spiral of copper tube, $\frac{1}{4}$ in. square, and the cheeks are built up of brass sheet and fitted with internal baffles compelling the water to flow in a tortuous path from the centre to the outside edge. Each member of the assembly—viz. each cylindrical core and each cheek—receives a separate supply of water through its own control cock from a distributor

pipe, and discharges into a common collector trough. Thus, by individual control of the different elements of the cooling system, very effective and economical cooling is possible.

The coils are wound with 0.048-in. single-cotton-covered copper wire. The turns are closely wound and are impregnated, the water-cooled bobbins being relied upon for cooling. The resistances of the coils are equal, and when running at full excitation the coils are paralleled and fed from the 240-volt mains, the power-dissipation being 2.75 A. per coil when hot, or a total of 11 A.—equivalent to 2.64 kW. Each of the smaller coils has 5700 turns, and each of the larger 6000; thus the maximum excitation is 64,400 ampere-turns.

For the work carried out so far, adequate excitation has been obtained by wiring the two outer coils in series with each other and in parallel with the inner coils; this effects economy in current-consumption, but leaves the full voltage applied to the coils nearer the gap.

§ 3. PERFORMANCE OF THE MAGNET

The magnet was found to show a very satisfactory saturation effect; figure 3 shows an (I, H) curve for one of the experimental pole-piece arrangements (see later).

Temperature rise of pole-pieces. A test was made in which a thermometer was placed in contact with the face of one of the pole-pieces, and carefully lagged to prevent loss of heat to the atmosphere. The maximum temperature-rise recorded after a long run at maximum excitation was only 3° C.

§ 4. FORCE-DISTRIBUTION

The observations of the distribution of the force $H \cdot dH/dx$ with the new magnet formed a crucial test of the general applicability of the new method, since this represented the first test of the latter on any magnet other than that used in the original development work, and the first test with saturated pole-pieces.

The pole-piece system which had been used for susceptibility-measurements with the old magnet* was transferred to the new one, and an exploring trolley similar to that described in one of the earlier papers† was used to measure the force-distribution along the axis of symmetry of the field. Figure 2 shows the results obtained for various magnetizing currents, and figure 3 the corresponding parts of the saturation curve.

The first curve, for a current of 1.5 A.—i.e. on the steeply rising part of the curve—corresponds to the conditions under which the old magnet had always to be operated, and it will be seen that this curve is practically identical with that obtained when the same pole-piece system was used on that magnet‡. This result is of great importance as the first evidence of the reproducibility of the method.

* *Proc. Phys. Soc.* 44, 275 (1932).

† *Proc. Phys. Soc.* 43, 383 (1931), figure 1.

‡ *Loc. cit.* figure 1.

The next curve, for 2.5 A., corresponds to the shoulder of the saturation curve, and is of definitely changed shape; the two following curves, for 6 and 12 A. respectively, correspond to operation at saturation, and the force-distribution is changed completely, although these two curves are similar to each other.

The progressive change in the shape of the curves is very similar to the change brought about by a progressive decrease in diameter of the flat pole-piece, as may be seen by comparison with earlier curves*. This suggests that by using a slightly larger flat pole-piece, it might be possible to reproduce the flat distribution curve when working at saturation, and tests in which the same concave pole-piece was used in conjunction with larger flat ones showed that this was indeed the case.

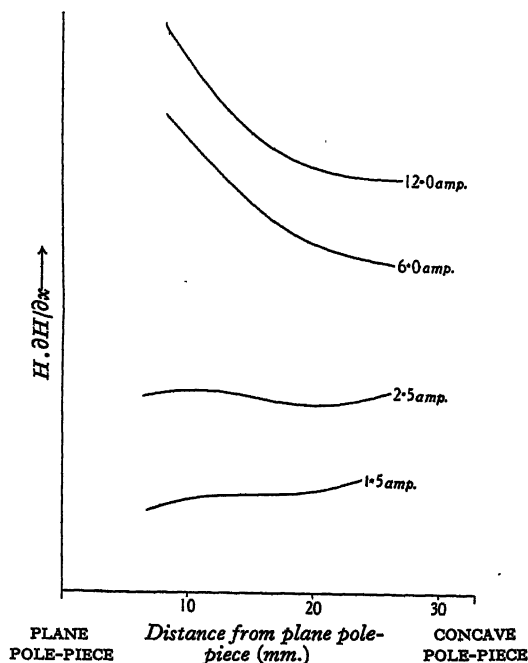


Figure 2. Force-distribution for various magnetizing currents.

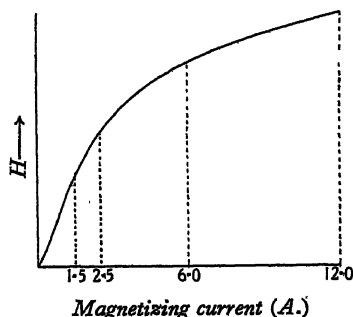


Figure 3.

Figure 4 shows some force-distribution curves obtained at saturation with the same concave pole-piece and the same gap as in the experiments just described, but with flat pole-pieces of different diameters. The distribution obtained with the 56.9-mm. flat is almost identical with that of figure 1 of the 1932 paper, the best distribution realized with unsaturated pole-pieces, and is that finally adopted for susceptibility-measurements with the new magnet.

We thus have the important result that working at saturation involves no change in the principle of the new method, or in the method to be adopted for choosing suitable pole-pieces; the only change as compared with the earlier work is that the optimum diameter of the flat pole-piece to be used with a given concave one at a given gap is slightly different.

* *Proc. Phys. Soc.* 43, 383 (1931), figure 7.

§ 5. APPARATUS FOR SUSCEPTIBILITY-MEASUREMENTS AT HIGH TEMPERATURES

The torsion-balance T-tube used for measurements at room temperatures and illustrated in figure 2 of the 1932 paper formed the nucleus of the apparatus for high-temperature work, but whereas in the earlier work it had been found convenient to mount the tube permanently in position on the electromagnet, so that the container for the specimens was always in its correct position relative to the magnetic field, it now became desirable to be able to remove and replace the torsion balance for the purpose of changing specimens. This was mainly due to the fact that owing to the much greater diameter of the windings of the new magnet, the space between the pole-pieces was much less readily accessible than had been the case with the old design.

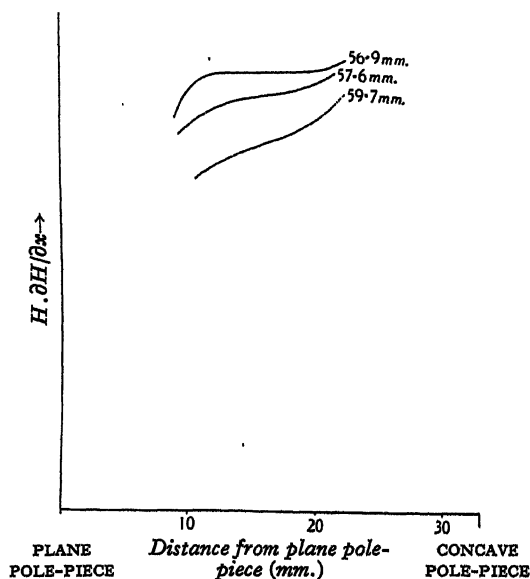


Figure 4. Force-distribution with flat pole-pieces of various diameters.

A new form of mounting had therefore to be devised, which would make it possible to remove the balance by a simple operation, and permit it to be replaced in exactly the same position relative to the field.

The arrangement adopted is illustrated by figure 5. The whole arrangement had to be designed to fit into a space 2.5-in. wide between the 18-in. diameter cheeks of the coil bobbins; it was provided with adjustments allowing the T-tube to be moved in any direction in order to make the initial adjustment to the correct position relative to the field; once this had been done, the controls could be locked, and the balance system could then be removed and replaced in exactly the same position by the operation of one easily accessible wing nut.

The main support consisted of a member, figure 5, comprising upper portions *A* and lower portions *G* working in sliding relation, to allow an adjustment for height; when this adjustment had been made the slides were locked by means of the screws *D*. This assembly was bolted, with screws passing through slotted holes in its feet, to the base of the magnet; the provision of these slots allowed an adjustment laterally—i.e. in a direction parallel to the axis of symmetry of the magnetic field. To the top of the frame was attached, by means of screws *F* passing through slots, a flat bar *E*, so that it was capable of adjustment in a direction perpendicular to the axis of the field.

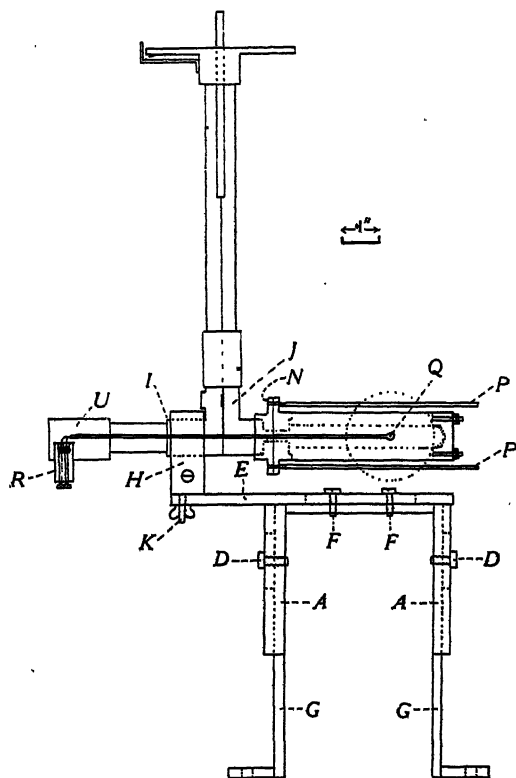


Figure 5. General view showing set-up of apparatus.

A brass block *H* was clamped to the brass part *I* of the torsion-balance T-tube *J*, as is seen in figure 5. From the base of this block projected a threaded stud *K* and two short pins, which fitted into corresponding holes at the end of the bar *E*. The engagement of these three projections with the corresponding holes ensured that the T-tube could always be attached to *E* in the same position, and it was clamped in this position by means of a wing-nut on the screwed stud.

The whole system was rigidly built up of brass bars of generous cross-section, to ensure that no distortion should be caused by the weight of the T-tube system, and it will be seen that the facilities provided for adjustment in three directions permitted the T-tube to be adjusted to a correct initial position, after which it

could readily be removed and replaced by removal of the wing-nut, which was easily accessible from the front of the magnet.

The furnace. The designing of a furnace for heating the specimens to high temperatures was a matter of some difficulty; its dimensions were strictly limited by the need for working with as small as possible an interpole gap but, at the same time, lagging had to be very effective to prevent heating of the pole-pieces; further, in the use of a horizontal furnace, there was a danger that convection currents might disturb the torsion balance and also prevent the attainment of steady, uniform temperatures in the furnace tube.

It was, however, found possible to build a horizontal furnace which behaved in a thoroughly satisfactory manner; its construction is illustrated by figure 6. The furnace tube *L* is a quartz test-tube measuring 10 cm. in length by 1.2 cm. in external diameter, on the outside of which the heater is wound. The tube is cemented firmly in position in a housing consisting of the copper tube *M* and sindanyo end-plates *N*, the space between the winding and the copper tube being filled with a lagging of

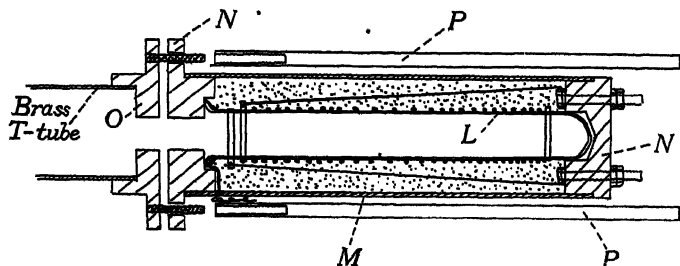


Figure 6. Section through furnace.

powdered magnesia. Sindanyo (a patent asbestos and cement board) was used because this material has very good thermal and electrical insulating properties, and can be machined accurately to any desired form. The sindanyo flange *N*, and the corresponding flange *O* which is permanently attached to the brass tube of the torsion balance, are arranged so that when the furnace is bolted to the T-tube by the bolts *P*, the only communication between the T-tube and the interior of the furnace is by way of the narrow tunnel bored through the centre of the flanges. This effectively prevents convection currents or excessive loss of heat from the furnace mouth. The arrangement of the sindanyo flange on the end of the brass T-tube also protects it from the hot part of the furnace, and prevents loss of heat to it by conduction.

The heater winding is of gauge-30 eureka wire; this material is slightly paramagnetic, having a measured susceptibility at room temperature of 8×10^{-6} . The winding comprises about fifty turns, wound bifilarly and more closely at each end of the tube than in the middle, in order to compensate for heat-losses at the ends, and to give a more uniform distribution of temperature along the tube. The winding is terminated by clamps of thin sheet copper, and as a protection is covered with a thin coating of alundum cement, which was found to have a susceptibility of $+9 \times 10^{-6}$.

The inside of the test tube is coated with a layer of copper about 0.5 mm. thick; this serves the double purpose of rendering the temperature-distribution more uniform, and of acting as an electrostatic shield between the furnace winding and the torsion-balance arm. The application of this metallic coating with a sufficiently uniform thickness presented some difficulty; the inner surface of the tube was first rendered conducting by applying a coating of aquadag (a colloidal graphite solution prepared as a lubricant for wire drawing), and after drying, baking at a low temperature, and polishing with a wad of cotton wool; this gave a very thin, highly polished coating of graphite, which served as a basis for the next process of electrolytic deposition of copper. Great care was necessary, in the initial stages of the deposition, to ensure a sufficient uniformity in the thickness of the deposit, but once a thin, uniform covering of copper had been obtained, it was easy to build up the thickness. Finally, a thin protective coating of platinum was electrolytically deposited.

Figure 5 shows how the furnace, bolted to the rear limb of the T-tube, fits between the pole-pieces of the magnet. When it is in position, there is a gap of about 1 mm. between each pole-piece and the furnace wall, and a thick sheet of mica is slipped into each of these gaps in order to protect the pole-pieces from heating by radiation or convection.

This arrangement, in combination with the water cooling of the magnet, is so effective that when the temperature in the interior of the furnace is at its maximum value of some 450° C., the temperature of the pole-pieces does not rise by more than a few degrees. An observation was made in which a small thermojunction was placed in contact with the flat pole-piece at the point where it is only separated from the furnace wall by the mica sheet; at this point the heating of the pole-pieces must be at a maximum. The measured rise in temperature when the furnace had been running at its maximum temperature for a long time was only 8° C., so that the mean temperature rise of the iron will certainly be of a negligibly small order.

The maximum temperature which can be reached with this eureka-wound furnace is, as just stated, some 450° C. This is a convenient range, since firstly the range of temperatures is also just that which can be covered with a base-metal thermocouple of fairly high voltage-output; and secondly, in the measurements which have been made of susceptibilities of nickel salts, it enables the behaviour of most simple salts to be studied up to their points of decomposition.

It is anticipated that no difficulty would be experienced in extending the measurements to considerably higher temperatures by using a furnace wound with platinum or a suitably high temperature alloy working above its Curie point, the eureka-wound furnace being retained for work at the lower temperatures. The design of the apparatus is such that furnaces are rapidly interchangeable.

Temperature-distribution. In the work of developing the furnace, a number of experimental models having differently spaced windings were wound, with the object of determining the best disposition of the turns to correct for end losses and produce a uniform temperature-distribution. For exploring the temperature-distribution in these and in the final model, as nearly as possible under working con-

ditions, a dummy torsion-balance arm was built up, carrying a thermocouple, the junction of which was contained in a small glass bulb simulating the specimen.

Figure 7 shows how, in the final form of furnace, the temperature varied along the tube for different values of heating-current. The temperature was found to be practically constant over any cross-section of the tube.

It will be seen that for every value of heating-current, a sufficiently extensive region of uniform temperature exists; at the maximum current, the temperature is constant within 1 per cent over some 15 mm. Furthermore, this region of uniform temperature always occurs at the same part of the furnace, whatever the value of the heating-current, its centre being at about 39 mm. from the closed end. Hence the apparatus had to be assembled so that the specimen whose susceptibility was to be measured always occupied that position.

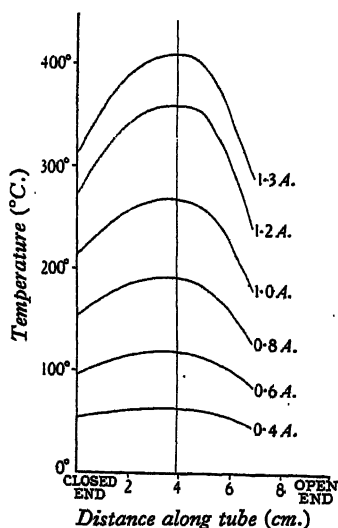


Figure 7. Temperature-distribution along furnace tube for different heating-currents.

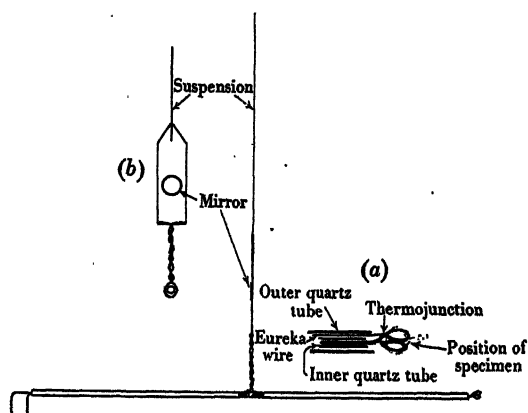


Figure 8. Suspended system of the torsion balance: (a) details of clamp for specimen, (b) front view of supporting stirrup.

The torsion balance. The torsion balance for high-temperature work was so designed that a thermocouple for measurement of the temperature of the specimen formed an integral part of it; its construction is illustrated by figure 8. The balance arm consists of a quartz tube about 1.5 mm. in diameter; through this passes a length of 30 s.w.g. silver wire terminated at one end by being bent into two small loops in parallel planes, which act as a clamp for the small bulbs containing specimens of the materials whose susceptibilities are to be measured. To one of the loops is silver-soldered a fine (36 s.w.g.) eureka wire, which is also led out inside the quartz tube of the balance arm, insulation between the two wires being provided by a finer concentric quartz tube slipped over the silver wire. This combination constitutes a thermocouple which, since it has its junction on a silver loop encircling the specimen, can be relied upon to give a reading which is a true measure of the temperature of the latter. At the other end of the arm the thermocouple wires are

bent over at right angles, to make contact with the mercury cups to be described later.

The arm is supported by a stirrup built up of copper wire and thin copper sheet, attached to its centre with shellac varnish; to the upper end of this the suspension is attached. In most of the work, a phosphor-bronze suspension strip (a galvanometer suspension) was used, but in some experiments a quartz fibre was substituted. It was attached by solder after its ends had been platinized with oil of platinum, coppered electrolytically, and tinned with molten solder, a zinc-chloride flux being used.

The exterior surface of the quartz tube of the balance arm was rendered conductive by means of a thin covering of metallic platinum, applied by coating with oil of platinum, drying, and baking. This coating is in conducting communication with the metal stirrup, and hence via the phosphor-bronze suspension with the metalwork of the T-tube, but is isolated from the wires of the thermocouple. Its purpose is to eliminate electrostatic attractions, as will be explained more fully later.

Figure 5 shows the assembly of the apparatus. It can be seen how the furnace is slipped over the specimen *Q*, and bolted to the sindanyo flange *N* on the end of the T-tube. The length of the arm of the balance is so chosen that, when the apparatus is assembled, the specimen occupies a position at 39 mm. from the closed end of the furnace tube, which, as has already been explained, is the optimum point for uniformity of temperature.

There is not much room for movement of the specimen in the narrow furnace tube, and it was therefore impossible to continue to determine the force acting on the specimen, when the field was applied, by allowing the balance to twist until equilibrium was reached, and measuring the deflection; the method of observation had to be modified by fitting a graduated torsion head and determining the twist necessary to restore the apparatus to its initial position. This adjustment to the initial position was judged accurately by reflection of a light-spot from a mirror carried on the copper stirrup supporting the balance arm.

It is arranged that deflections are generally of the order of three complete revolutions—i.e. 1080° . On the torsion head, which is 10 cm. in diameter and graduated in degrees, a fraction of a degree can easily be estimated, and no difficulty is experienced in reading the deflection to within 0.1 per cent. The actual observation could, in fact, be made with greater accuracy, but this would not represent such accuracy in the susceptibility-measurement, because of slight elastic after-effects in the suspension, and imperfections in the set-up of the apparatus.

At the forward end of the T-tube can be seen the arrangement for making contact between the thermocouple wires and the external bridge circuit; the details will be appreciated by reference to figure 9.

The essential part of the apparatus is an ebonite block *R* from which part is cut away as shown. Three saw-cuts *S* were made, and between each pair of cuts a hole was drilled through to the base of the block and tapped to take a 4 B.A. screw *T*. A sheet of mica was slipped into each cut and cemented in position with shellac varnish; in the cut-out part of the block the space between these mica sheets forms

two small cells which are used as mercury cups, electrically insulated from each other but in good thermal communication, since they are separated only by a thin sheet of mica. With screws *T* inserted in the tapped holes, and screwed in fully, the cups are filled with mercury, the dimensions of the cups and the threaded holes being such that when the screws are unscrewed nearly to their fullest extent, the mercury runs down into the threaded holes in the ebonite leaving the cups empty.

The position of the block at the end of the T-tube is such that the turned-down ends of the thermocouple wires come into the mercury cups. When it is desired to make a measurement of temperature, the screws are screwed up to fill the cups with mercury, making contact between these wires and silver and eureka leads connecting the cups with the cold junction and the bridge circuit. When an observation of magnetic force is being made, the cups are emptied by withdrawing the screws to the necessary extent, and the ends of the thermocouple wires then swing freely in the empty cups.

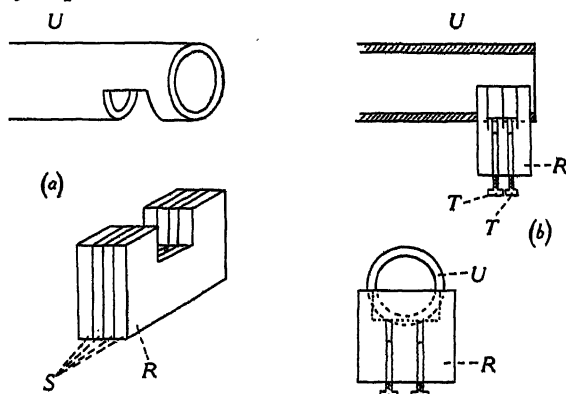


Figure 9. Thermocouple contact block. (a) Perspective view of brass tube and ebonite block, before completion. (b) Section and front elevation of completed apparatus.

The ebonite block *R* is supported in a massive tube *U* of brass, and this, combined with the fact that the cups are in good thermal contact through the thin sheet of mica separating them, ensures that no appreciable difference exists between the temperatures of the cups.

The cold junction is kept in ice. After having been set up, the thermocouple was very carefully calibrated with reference to standard fixed points; over the range 0–100° C. calibration was effected by comparison with a standard mercury thermometer. After the torsion balance had been set up, direct fixed-point determinations could not conveniently be made. The calibration was therefore checked from time to time by comparison with another calibrated thermocouple, and was found to be maintained in a perfectly satisfactory way; measurements of the output voltage of the couple were made on a specially constructed slide wire bridge.

In order to guard against the introduction of parasitic electrostatic forces acting on the torsion balance, the whole of the metalwork—torsion head, thermocouple contact tube, T-tube, metallized torsion balance arm, and internal shield of the furnace tube—was bonded together and earthed.

§ 6. METHOD OF OBSERVATION

It should be clear from the foregoing descriptions that one of the main features of this apparatus and method is that a tiresome adjustment of each specimen is replaced by one initial adjustment of the apparatus, so that when once this has been effected, the different specimens can be slipped into position on the torsion balance and observations can immediately be commenced. This initial adjustment of the apparatus is obviously of fundamental importance, and must be carried out with care.

Two main adjustments have to be made when the apparatus is set up. (i) The torsion balance must be so mounted that the specimen always occupies a position on the axis of symmetry of the field, and in the region of uniform force. (ii) The furnace must be so related to the torsion balance that the specimen always occupies a position in the region of maximum uniformity of temperature.

As has been explained in the preceding section, the latter condition is satisfied when the apparatus is being built, by a suitable choice of the length of the arm of the torsion balance. In making the initial adjustment to satisfy the first condition, a specimen was placed in position on the torsion balance, which was mounted in position between the pole-pieces of the magnet. By adjusting a wire rider on the forward part of the balance arm, the arm was set in a horizontal position; and by means of the various adjustments provided on the torsion-balance support, the specimen was brought to a position at the centre of the axis of symmetry of the field, the torsion head being set so that the balance arm settled along the axis of the horizontal arm of the T-tube. The lamp and horizontal scale system used for setting the zero of the torsion balance was now set so that the spot indicated zero on the scale, and all the controls were locked. If now the torsion balance was removed and replaced, or the specimen changed, any displacement from the axis of symmetry in a vertical direction was indicated by the spot shifting to a position above or below the scale.

With the furnace in position over the specimen, the latter's movements were restricted to a matter of some 3 mm. on each side of the mid-point of the gap, which, as can be seen from an inspection of figure 4, meant that it was confined to the region of uniform force. Thus it was only necessary, in setting a specimen, to slip it on to the end of the torsion balance so that it was clamped in position between the two silver loops, bolt on the furnace, place the whole apparatus in position on the electromagnet, and adjust the rider to bring the light spot on to the scale.

Owing to slight differences in the sizes of the specimens, the distance between the centres of the specimen and the torsion balance arm—i.e. the true arm of the couple measured—was liable to slight variation. These variations were, however, never more than 0.5 mm., the length of the arm being 113 mm. A correction was applied, and was of the order 0.5 per cent.

As containers for the specimens, small quartz bulbs some 3 mm. in diameter were used. In some cases it was necessary to seal off the necks of the bulbs, and glass was then substituted, as it was not found possible to seal a quartz bulb without

damaging the contents by heat. A blank experiment was in every case performed on the empty bulb, in order that a correction might be applied for the magnetism of the bulb and balance arm over the temperature-range concerned. This correction amounted in general to some 5 per cent. After this experiment had been carried out the bulb was filled with the powdered salt, weighed, sealed if necessary, and replaced on the torsion balance; measurements of susceptibility at various temperatures were then proceeded with.

When susceptibility-measurements were being made the procedure was as follows: the specimen having been inserted and the apparatus placed in position on the magnet, the rider was adjusted to bring the light spot on to the scale, which indicated that the specimen was on the axis of symmetry of the field. After verifying that the balance arm was swinging freely, the readings of the torsion head and light spot were noted. The field was then applied, and the torsion head turned to restore the light spot to its initial position; thus the twist necessary to compensate for the magnetic couple was determined. The field was then switched off and the torsion head restored to the zero position; the heating-current was switched on at some predetermined value and the mercury cups were filled to connect the thermocouple to the bridge circuit. Thus the temperature of the specimen could be measured, and when it had reached a steady state the mercury was withdrawn from the cups so that the balance arm could swing freely, and another twist-measurement was made as before. The heating-current was then set to a higher value, and the observations were repeated. Proceeding in this way, a series of twist-measurements was made over the range of temperature desired.

The measurements were corrected for the twist necessary to compensate the forces acting on the bulb and the balance arm by applying the results of the preceding experiment on the empty bulb.

Now we have, if the corrected twist be θ ,

$$\begin{aligned}\text{Couple acting on the specimen} &= n\theta \\ &= rm\chi H \cdot \partial H / \partial \chi,\end{aligned}$$

where n is the restoring couple of suspension per unit twist;

r the arm of couple;

m the mass of specimen; and

χ the susceptibility of specimen.

Thus

$$\chi = \frac{n}{rH\partial H/\partial \chi} \cdot \frac{\theta}{m} = K \cdot \frac{\theta}{m},$$

where K is a constant characteristic of the apparatus. All results are therefore expressed in terms of θ/m , conveniently expressed in "degrees of twist per milligram." These values are proportional to the susceptibilities, and can be converted to susceptibility-values when K is known. K can be determined from the known constants of the apparatus, but this is a somewhat involved process when accurate results are required, and it is preferable for most purposes to effect a calibration of the apparatus by the use of some substance whose susceptibility is already known with accuracy.

§ 7. MEASUREMENTS OF SUSCEPTIBILITIES OF SOME
NICKEL COMPOUNDS

Anhydrous nickel sulphate. This compound has been examined over the range 14–290° K., by L. C. Jackson*, who found that over the upper part of this range it followed a Curie-Weiss law with θ equal to -79.4° , and p to 16.9 Weiss magnetons. Honda and Ishiwara† made observations up to the temperature of decomposition (about 800° C.) and found that the (χ^{-1}, T) curve showed a slight downward curvature.

More recently, Cabrera and Duperier, and Mlle Serres‡ have suggested that the less simple law

$$(\chi - a)(T - \theta) = C$$

will explain the behaviour of the salt at high temperatures, and Serres assigns to a the value $425 \cdot 10^{-6}$, without, however, giving more detailed numerical results.

In the present work, observations have been made over the range 290–550° K. The material used was prepared from a pure heptahydrated sulphate, which, after recrystallization a few times from conductivity water, was dehydrated by being heated in a quartz vessel in an electrically heated quartz tube furnace. After the quartz bulb in which the specimen was introduced into the magnetic field had been filled, it was again heated for a time in order to remove any water acquired during the filling operation. Two samples of the hydrated sulphate were obtained, these being from entirely different batches received from the manufacturer.

The results of the observations were very consistent; curve *A* of figure 10 shows the results for a specimen from each batch, and it will be seen that they are in excellent agreement.

In the absence of an accurate calibration of the apparatus, absolute values have been assigned to the susceptibilities by adjusting the observed relative values to agree with Jackson's value at 290° K. This leaves a little uncertainty as to the exact value of χ , but it allows a test to be made of the manner in which the expression of Mlle Serres expresses the nature of the variation of χ with T .

The results of Honda and Ishiwara over the temperature range concerned are also shown on the curves; these are seen to be in very good agreement, giving good justification for the calibration adopted.

It is obvious that the curve showing the relation between χ^{-1} and T shows a concavity towards the T axis, indicating a departure from a true Curie-Weiss law. In order to determine whether a relation of the form suggested by Serres, viz.

$$(\chi_m - 425 \cdot 10^{-6})(T - \theta) = C,$$

will explain this departure, a second curve *B*, figure 10, has been prepared, showing the relation between $1/(\chi_m - 425 \cdot 10^{-6})$ and T ; it will be seen that this gives a good linear relation, and it may be concluded that the observations are in good agreement with the law suggested by Mlle Serres.

* *Phil. Trans. A* 224, 1 (1923).

† *Sci. Rep. Univ. Tohoku*, 4, 215 (1915).

‡ *Bull. Soc. Franç. de Phys.* 4, 74 (1933).

The value of θ indicated by the curve is -58° ; and on the basis of the calibration in terms of Jackson's figures, the value deduced for the magnetic moment p of the carrier from the value of C in the above expression is 16.0 Weiss magnetons.

Table 1 has been reproduced to show the manner of reducing the results; it refers to specimen a of the curves.

Table 1

$T(^{\circ}\text{K.})$	A ($^{\circ}$)	B ($^{\circ}$)	C ($^{\circ}$)	D	χ_m	χ_m^{-1}	$\chi_m - 42 \cdot 10^{-6}$	$(\chi_m - 42 \cdot 10^{-6})^{-1}$
294.0	823	815	818	40.9	0.00412	243	0.00379	270
312.7	779	776	779	39.0	0.00393	254	0.00351	285
351.6	701	705	708	35.4	0.00356	281	0.00314	318
403.0	629	641	643	32.2	0.00324	309	0.00282	355
458.0	563	582	584	29.2	0.00294	340	0.00252	397
502.0	516	539	541	27.1	0.00273	366	0.00231	433
554.4	474	501	503	25.2	0.00254	394	0.00212	472

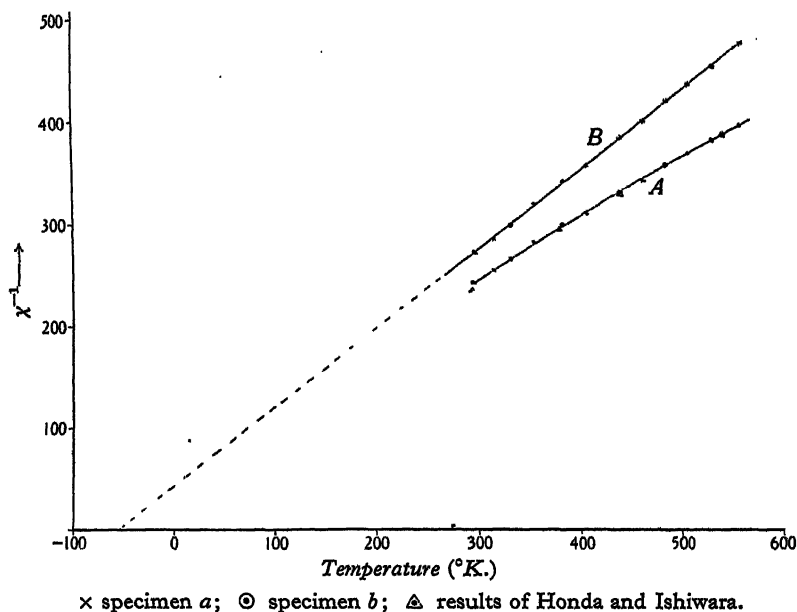


Figure 10.

Column A gives the observed twist, as explained on p. 226. B gives this value corrected for the twist needed to compensate for the magnetism of the bulb and support. In column C the further small correction for variation in the arm of the couple, explained on p. 225, is applied. In column D this value is reduced to a relative susceptibility in terms of twist per milligram by dividing by the weight of the specimen; and this is brought to a true susceptibility, on the basis of Jackson's figures, in the next column.

Nickel cyanide. The properties of this salt are particularly interesting, and it had already been selected for a special examination. It is known that the susceptibility

of the hydrated salt is of the same order of magnitude as those of other simple nickel salts, but that on dehydration its value decreases very considerably*. Bose has suggested that "on complete dehydration the compound would be found to be diamagnetic." On the other hand, Mlle Serres† finds that the anhydrous cyanide is paramagnetic and "seems to obey a Weiss law without correction for a constant paramagnetism."

For this work, samples of the cyanide were prepared by precipitation, carefully prepared solutions of nickel acetate and potassium cyanide of AR quality being used. The precipitate was thoroughly washed, and dried at 100° C. It was then found to contain 23.11 per cent of water, which corresponds to a formula $\text{Ni}(\text{CN})_2 + 1.85 \text{H}_2\text{O}$ and points to a partly dried dihydrate.

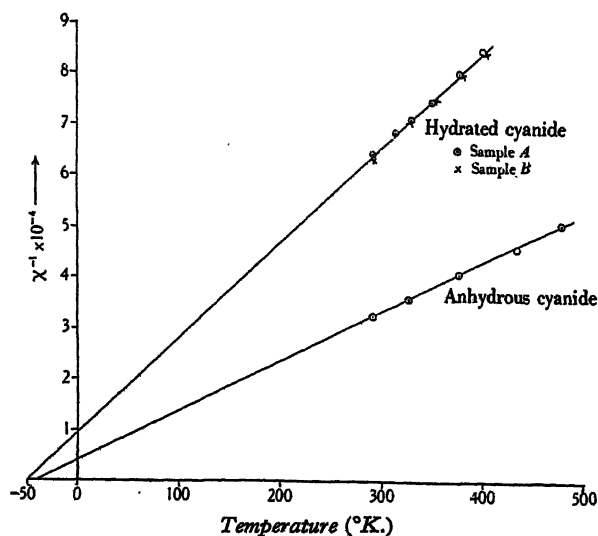


Figure 11.

Measurements on hydrated salt. Measurements were made on several samples of this compound, with consistent results; observations were made on samples in both open and sealed bulbs, the latter in case any dehydration might be occurring at the higher temperatures, but it was found that similar results were obtained in each case. In the curves of figure 11, results are given for a sample contained in a closed bulb (A) and an open one (B); the χ^{-1} results are a trifle higher for A than for B, but the general agreement is entirely satisfactory. The reduction to absolute values is here again based on Jackson's figures for the anhydrous sulphate. A Curie-Weiss law is followed with T equal to -50° , and the magnetic moment of the carrier, evaluated on the basis of the composition $\text{Ni}(\text{CN})_2 + 1.85 \text{H}_2\text{O}$, is 12.3.

Measurements on anhydrous salt. In examining this compound, two methods were available. (i) An open-necked bulb was filled with the hydrated cyanide, and placed

* Bose, *Nature*, 125, 708 (1930); Fereday, *Proc. Phys. Soc.* 44, 279 (1932).

† *Loc. cit.*

in position in the torsion balance; observations of susceptibility were made at temperatures up to just above the point of dehydration (about 200°C.). The temperature being kept constant (susceptibility, time) observations were then made, and these enabled the dehydration process to be followed until the attainment of a constant value indicated complete dehydration. Measurements of the susceptibility of the dehydrated salt were then made at successively lower temperatures down to room temperature. (ii) A glass bulb was filled with the hydrated cyanide, which was then dehydrated in the torsion balance as before. By effecting dehydration in this way, a very close control could be exercised. When dehydration was complete the bulb was removed and its neck was immediately sealed by the application of a fine, pointed blowpipe flame. It was then replaced in the torsion balance for the purpose of making the susceptibility-measurements.

A number of observations were made by each method, and good agreement was obtained. The second method proved the more satisfactory, however, since with an open-necked bulb there was a tendency for rehydration to occur at the lower temperatures, resulting in a slight increase in susceptibility.

A specimen (χ^{-1} , T) curve is reproduced in figure 11. The sample to which this refers was prepared by dehydration and sealing of the hot bulb. It is seen quite definitely that the anhydrous salt behaves as a normal paramagnetic, following a Curie-Weiss law; and definite values can be assigned to the constants θ and p . θ is seen to have the value -42° ; and p , calculated on the basis of the formula $\text{Ni}(\text{CN})_2$, is 4.75 Weiss magnetons.

§ 8. ACKNOWLEDGMENTS

The very satisfactory performance of the electromagnet used for this research is due almost entirely to the interest of the Research Staff of the Metropolitan-Vickers Electrical Co., who designed and built the magnet, and I should like to take this opportunity of expressing my appreciation of their assistance.

I am indebted to Prof. H. R. Robinson for the facilities which he has placed at my disposal in the Physical Laboratories of the East London College; and to the Department of Scientific and Industrial Research, who have supported the work by a Senior Research Award.

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THE THEORY OF THE MICROSCOPE, II: DARK-GROUND ILLUMINATION

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ABSTRACT. This paper applies the methods developed in a previous paper* to the discussion of the effects in dark-ground illumination when the image of the source of light is projected into the object plane by an illuminator of the symmetrical type. The treatment is two-dimensional. The conditions necessary for the formation of genuine and spurious images are investigated, and it is shown that the Abbe principle is theoretically valid in the cases considered. A short practical investigation with Grayson's rulings supports the theoretical conclusions, but indicates the desirability of closer examination of the causes of misleading interference phenomena.

§ 1. SCOPE OF THE PRESENT INVESTIGATION

A PREVIOUS paper on the theory of the microscope effected the analysis of the mode of the image-formation for non-self-luminous objects in a manner distinct from that used by Abbe. If the object is illuminated by light focused by a condenser so that the image of the source falls in the image plane, the distribution of illumination due to any elementary point of the source becomes known, and it is possible to calculate the distribution of illumination in the posterior focal surface of the objective when the object consists of a series of equidistant apertures. Further steps in that paper effected the calculation of the interference phenomena in the final image plane; firstly those due to a single point of the source, and finally the complete effect due to an extended source of light. The treatment throughout was two-dimensional.

In recent years great importance has been attached to the dark-ground method, in which the object is illuminated from the condenser by oblique rays with numerical apertures greater than that of the objective. The light can only reach the image by the effects of reflection, refraction, or scattering, in which the path of the energy may be partly deflected into the objective. The phase relations of the intercepted vibrations have an essential bearing on the actual distribution of light into the optical system.

The scope of the present investigation is to extend the methods described above to the case of dark-ground illumination, and to discuss how far the results may be applied to practical cases. The problem has been discussed by M. J. Cross† on the basis of the Abbe principle, but his assumption of an oblique illumination by a

* *Proc. Phys. Soc.* 43, 186 (1931).

† *Knowledge*, 1912, p. 37.

narrow parallel beam of light seems artificial at first sight, since most modern dark-ground illuminators give an illuminating beam of a conical character, or rather a beam contained between two cones, and yield an image of the source of light in the image plane. Although the three-dimensional case presents undue difficulty, it is possible to give a discussion of the two-dimensional case which resolves some of the difficulties.

Consider one point only of the source of light B , figure 1. The condenser, which will be first supposed to give an unrestricted beam, focuses this in the object plane. Let the illuminating beam have a maximum numerical aperture A_2 , let the radius of the wave surface (of circular section) as it leaves the condenser be f , and let the amplitude be a . The discussion must be limited to the case in which the maximum numerical aperture is small.

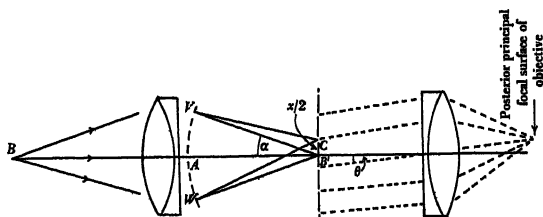


Figure 1.

Consider the amplitude, in the neighbourhood of the image point B' , contributed by an element of the wave surface at V from which the ray VB' makes an angle α with the principal ray AB' . The width of the element of the wave surface subtending an angle $\delta\alpha$ is $f\delta\alpha$ and the gross amplitude contribution δs at B' is therefore given by

$$\delta s = \frac{a}{\lambda f} \cdot f \delta\alpha.$$

There will be a contribution of equal numerical magnitude from the corresponding point symmetrically situated in the other half of the wave. If we consider vibrations occurring in the plane of the diagram, it is clear that the resultant vibrations at B' will be polarized in directions inclined to the image plane at angles $+\alpha$ and $-\alpha$ respectively. The amplitude contributions of these components will therefore be subject to a correcting factor of $\cos \alpha$, since the resultant vibration must be in the image plane. Hence the net amplitude contribution δs for each of these vibrations is given by

$$\delta s = \frac{a}{\lambda f} \cdot f \delta\alpha \cos \alpha = \frac{a}{\lambda_0} \delta(n \sin \alpha),$$

where n is the refractive index of the space concerned, and λ_0 is the wave-length of light in a medium whose refractive index is unity. We may write the above expression, since $n \sin \alpha$ is A the numerical aperture,

$$\delta s = \frac{a}{\lambda_0} \delta A.$$

When we consider the vibration components perpendicular to the plane of the

diagram, we may recall that the amplitudes of all radiations reaching the image through the outer regions of any optical system are subject to uncertain losses through the more oblique reflections encountered by the marginal rays, and it would be very difficult to take account of such effects. We can be sure however that the $\cos \alpha$ reduction, taken for the vibrations as a whole, is quite in harmony with a possible case; it will approximate to unity under the condition that the angles involved are small. This will now be assumed.

Vibrations from V and W arrive at B' in the same phase, but at C , at a distance $\frac{1}{2}x$ from B' , the disturbance from V has a shorter path, while that from W has a longer one. The relative phase angles (x being very small) are

$$\pm \lambda_0^{-1} \pi n x \sin \alpha.$$

The amplitude s_0 due to the whole symmetrical wave of numerical aperture A_2 is given by

$$s_0 = \frac{2a}{\lambda_0} \int_0^{A_2} \cos \left(\frac{\pi x}{\lambda_0} A \right) dA,$$

but if the central regions of the wave are screened to produce symmetrical dark-ground illumination between numerical apertures A_1 and A_2 , the amplitude at C is now

$$\begin{aligned} s &= \frac{2a}{\lambda_0} \int_{A_1}^{A_2} \cos \left(\frac{\pi x}{\lambda_0} A \right) dA, \\ &= 2a (\pi x)^{-1} \{ \sin (\pi x A_2 / \lambda_0) - \sin (\pi x A_1 / \lambda_0) \}. \end{aligned}$$

Write $p = \pi x / \lambda_0$; then

$$s = 2a (\lambda_0 p)^{-1} \{ \sin (p A_2) - \sin (p A_1) \}.$$

In the same manner as that of the foregoing paper, we may now consider an object consisting of a series of equidistant apertures at relative distances x , and placed at distances $\pm x/2, \pm 3x/2, \pm 5x/2$, etc., from the centre point of illumination. These apertures will become the sources of disturbances having the same phases, but varying amplitudes given by the corresponding value of s in the above expression.

These vibrations are focused by the objective of the microscope, and we may consider the effects at points, in the principal focal surface behind the objective, corresponding to various directions of divergence from the normal through the point B' . For a small angle of diffraction, θ , from the normal to the object plane, the resultant amplitude for the first pair of apertures on either side of B' will be proportional to

$$4a (\lambda_0 p)^{-1} (\sin p A_2 - \sin p A_1) \cos \{ (\pi x n' \sin \theta) / \lambda_0 \},$$

where n' is the refractive index on the side of the object plane towards the objective.

The resultant from all the successive pairs of apertures is therefore given (when A_0 is written for $n' \sin \theta$) by:

$$\begin{aligned}
\text{Amplitude}_\theta &= \text{constant} \times 4a(\lambda_0 p)^{-1} \{ (\sin pA_2 - \sin pA_1) \cos pA_\theta \\
&\quad + \frac{1}{3} (\sin 3pA_2 - \sin 3pA_1) \cos 3pA_\theta \\
&\quad + \frac{1}{5} (\sin 5pA_2 - \sin 5pA_1) \cos 5pA_\theta + \text{etc.} \}, \\
&= \text{constant} \times 4a(\lambda_0 p)^{-1} \{ (\sin pA_2 \cos pA_\theta + \frac{1}{3} \sin 3pA_2 \cos 3pA_\theta \\
&\quad + \frac{1}{5} \sin 5pA_2 \cos 5pA_\theta + \text{etc.}) \\
&\quad - (\sin pA_1 \cos pA_\theta + \frac{1}{3} \sin 3pA_1 \cos 3pA_\theta + \frac{1}{5} \sin 5pA_1 \cos 5pA_\theta + \text{etc.}) \}, \\
&= \text{constant} \times 2a(\lambda_0 p)^{-1} [\{ \sin p(A_2 + A_\theta) + \frac{1}{3} \sin 3p(A_2 + A_\theta) + \text{etc.} \} \\
&\quad + \{ \sin p(A_2 - A_\theta) + \frac{1}{3} \sin 3p(A_2 - A_\theta) + \text{etc.} \} \\
&\quad - \{ \sin p(A_1 + A_\theta) + \frac{1}{3} \sin 3p(A_1 + A_\theta) + \text{etc.} \} \\
&\quad - \{ \sin p(A_1 - A_\theta) + \frac{1}{3} \sin 3p(A_1 - A_\theta) + \text{etc.} \}].
\end{aligned}$$

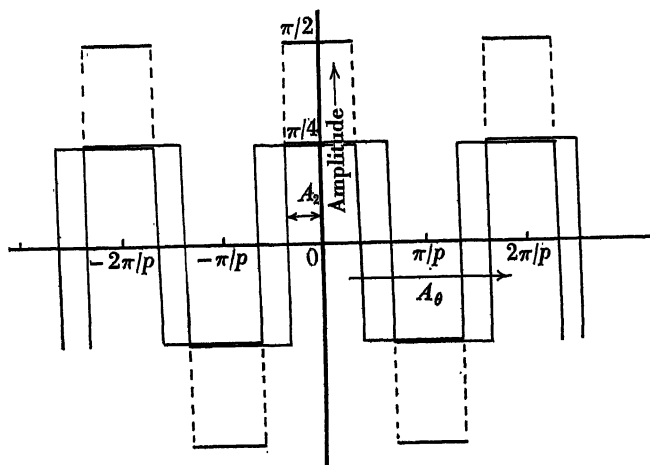


Figure 2.

In actual microscopical observations, objects of fine regular structure are often encountered. A diatom may have some hundreds of regularly spaced ribs or dots. A diffraction grating having 30,000 lines to the inch could easily be resolved by an objective of numerical aperture 0.65, and it is quite possible for, say, 1000 elements of the grating to contribute their effects towards the formation of the diffraction maxima in such a case. Practical considerations therefore suggest that cases of theoretical interest include those in which a very great number of terms in the above series are taken; and expressing the result of the series as its sum taken to infinity then involves only a slight error.

The first Fourier series in the brackets has, if an infinite number of terms be taken, corresponding to a great number of apertures, a value of $\pi/4$ from $p(A_2 + A_\theta) = 0$ to $p(A_2 + A_\theta) = \pi$, and a value of $-\pi/4$ when the same angle lies between π and 2π , and so on. The other brackets can be similarly interpreted. The first bracket is thus $\pi/4$ from $pA_\theta = -pA_2$ to $pA_\theta = \pi - pA_2$, and the second bracket is $\pi/4$ from $pA_\theta = pA_2$ to $pA_\theta = -(\pi - pA_2)$.

The first two series alone represent the case when the full aperture of the condenser illuminates the object plane. Their sum represents a series of isolated maxima (see figure 2) extending over regions corresponding to numerical apertures $\{-(\pi/p) \pm A_2\}$, $\{\pm A_2\}$, $\{(\pi/p) \pm A_2\}$, etc.; they constitute the diffraction maxima produced by the object. The range of numerical aperture of each maximum is equal to that of the condenser. The spacing of the maxima depends only on π/p , i.e. on λ_0/x . It is clearly seen that

$$n' \sin \theta = \lambda_0/x$$

is the usual condition giving the angle of diffraction of the first-order spectrum for normal illumination.

If the last two brackets in the full expression above are evaluated, they are found to give similar isolated maxima extending over the numerical apertures

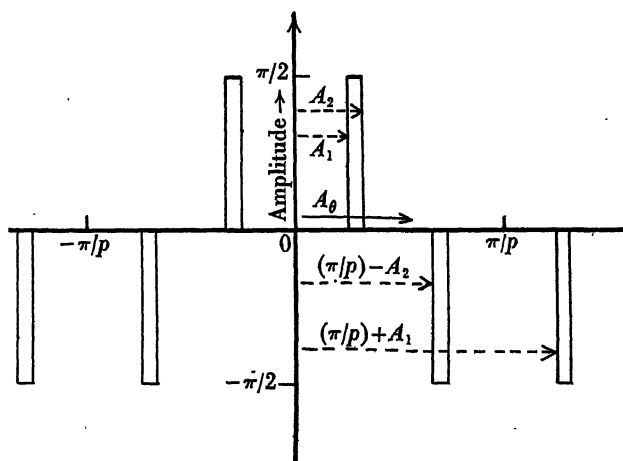


Figure 3.

$\{-\pi/p \pm A_1\}$, $\{\pm A_1\}$, $\{\pi/p \pm A_1\}$, and they have the opposite signs to the first two brackets. The final resultant therefore shows a succession of maxima symmetrically placed about the apertures $-\pi/p$, 0 , π/p , etc., the centres of the maxima being found at $\pm \frac{1}{2} (A_2 + A_1)$ on each side, and the width being $A_2 - A_1$ in each case. The maxima symmetrical about the centre correspond to the direct light from the condenser.

In the case of symmetrical dark-ground illumination the lower aperture A_1 of the illumination is greater than the aperture, A_ϕ say, of the objective, and the direct light cannot enter. We have, however, only to increase A_2 until

$$(\pi/p) - A_2 < A_\phi$$

before light from the first-order diffraction maxima on each side begins to enter the objective. This condition can be written

$$\pi/p < A_\phi + A_2$$

or

$$\lambda_0 < x(A_\phi + A_2).$$

If A_2 is only slightly greater than A_ϕ , then we shall have the approximate limiting condition that

$$\lambda_0 = 2x A_\phi$$

or

$$x = \text{grating spacing} = \lambda_0 / 2A_\phi,$$

and in this case symmetrical parts of the two first-order maxima of opposite sign will be just within the limit of the numerical aperture of the objective, one on each side. The condition is suggested diagrammatically in figure 4. In the ideal case which we have discussed, the light in all the maxima will be coherent, and there would (in the case of a single-point source of illumination) be reason to expect an interference effect which would be seen in the microscope as a succession of fringes of a frequency corresponding in this case very nearly to the resolution of which the objective is capable with direct oblique illumination. If, on the other hand, the spacing of the apertures is imagined to vary while the disposition of the illumination remains constant, the mean numerical aperture of the diffracted beams entering the objective will be $(\pi/p - A_D)$, where $A_D = \frac{1}{2}(A_1 + A_2)$. Now A_D is not very different from A_ϕ in the case being considered, so that

$$\pi/p - A_D = \pi/p - A_\phi \text{ approximately,}$$

and these beams will both take the axial direction when

$$\pi/p = A_\phi, \text{ i.e. when } A_\phi = \lambda_0/x.$$

There is evidently no correspondence between any possible interference effects from these first-order maxima and the spacing of the object elements, since the interference fringes will grow indefinitely broader as these maxima both approach the axis and coincide. It will thus be expected that even if any of the maxima can produce mutual interference effects, the fringes will not correspond in any way to the geometrical image.

On the other hand the obliquity of the cone of illumination from the condenser may be just great enough to allow corresponding first-order and second-order maxima on the same side both to enter the objective. If they enter symmetrically at apertures $\pm A_\phi$, the entry of the first-order maximum is represented by

$$-(\pi/p) + A_D = A_\phi \quad \dots\dots(1),$$

while the entry of the second-order maximum is represented by

$$-(2\pi/p) + A_D = -A_\phi \quad \dots\dots(2).$$

The condition is suggested in figure 5, but the beams are only shown as unilateral for simplicity. On subtracting the equations we find

$$A_\phi = \pi/2p = \lambda_0/2x,$$

i.e.

$$x = \lambda_0/2A_\phi,$$

so that once more a lens of numerical aperture A_ϕ could attain its full resolving power; but the same equations indicate that in order to attain this condition $A_D = 3A_\phi$, i.e. three times the numerical aperture of the objective. This case was worked out by M. J. Cross, but it has been judged worth while to re-state the

argument in the present connection. The separation of the interfering maxima is π/p , which only depends on the spacing of the apertures. The interference phenomena in the image correspond in frequency to the object (see below, p. 240).

A practical test such as that described below soon shows that the right-hand maxima will not give observable interference effects with the left-hand maxima under the ordinary conditions in the microscope, though effects of the kind could probably be observed with special apparatus. The reason for the non-appearance of the effects is explained by the theory given below.

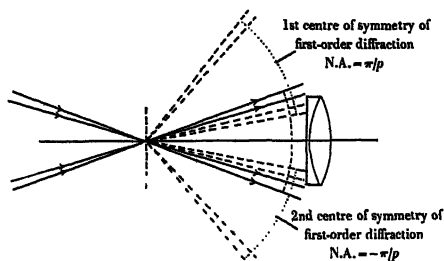


Figure 4.

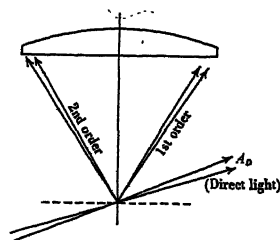


Figure 5.

§ 2. GENERAL THEORY OF THE DISTRIBUTION OF LIGHT IN THE IMAGE OF A SERIES OF APERTURES (BRIGHT-GROUND CASE)

With reference now to the first paper, an expression was given on page 198 for the phases and amplitudes of the maxima appearing in the back focal surface of the objective in the case when the object consists of a series of indefinitely narrow apertures lying at points defined by

$$u, u \pm v, u \pm 2v, \text{ etc.},$$

where v is a measure of the grating interval and u is a corresponding measure of the displacement of the maximum illumination, in the grating plane, from the central aperture of the grating. The symbol u actually represents a phase angle, being $2\pi h (NA_c)/\lambda_0$, where h is the linear interval corresponding to u , and NA_c is the numerical aperture of the cone of illumination from the condenser. The symbol v represents the corresponding phase angle expressing the measure of the grating interval π , i.e. it is $2\pi\pi (NA_c)/\lambda_0$. The numerical aperture NA_c will be written A_c for brevity in subsequent expressions.

The expression for the displacement is

$$(\pi/v) (1^* + \sum e^{is_r u^*}),$$

where $s_r = 2\pi\pi/v$, and the meaning of the *asterisk* is that each term is subject to the limitation that it only exists within the limits $m + s_r = \pm 1$; m is the measure of the obliquity of the diffracted light. It should be remembered that the expression should be multiplied by an infinitesimal quantity du , where du represents the width of a (very narrow) aperture, but this need not be written in the subsequent expressions unless it is desired to integrate for apertures of finite width.

Starting from this expression we may notice a method of deriving the amplitude in the final image which is more systematic than that given on page 203 of the original paper.

The result quoted above gives the amplitudes and phases of the maxima in a reference surface centred in that point B'' in the final image plane which is conjugate to the point of maximum illumination in the object plane; suppose that the complex $\phi(P)$ represents the amplitude and phase of the disturbance at a point in this spherical reference surface, corresponding to a numerical aperture A' equal to $n' \sin \alpha'$ on the image side. Now in the case of a uniform circular wave-front centred in B'' , figure 6, we can write the relative phase angle of the disturbance (from the region of the wave-front defined by the angle α') arriving at C'' in the image plane at a distance h' from B'' as

$$\lambda_0^{-1} 2\pi n' h' \sin \alpha' \quad \text{or} \quad \lambda_0^{-1} 2\pi h' A',$$

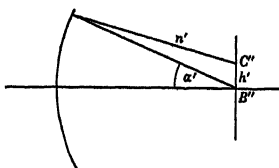


Figure 6.

where n' is the refractive index of the image space, and λ_0 is the wave-length of light in a medium whose refractive index is unity*. Hence, assuming the approximate correction factor of $\cos \alpha$ as above, the displacement at C'' due to the surface element is given (in terms of the exponential convention) by

$$\lambda_0^{-1} \phi(P) e^{i(2\pi n' A' / \lambda)} dA,$$

and the total effect produced by a region of uniform amplitude and phase $\phi(P)$ over a range of numerical aperture A_y to A_z is

$$\begin{aligned} \text{displacement} &= \frac{\phi(P)}{\lambda} \int_{A_y}^{A_z} e^{i(2\pi n' A' / \lambda)} dA' = \frac{\phi(P)}{2\pi i h'} (e^{i2\pi n' A_z / \lambda} - e^{i2\pi n' A_y / \lambda}), \\ &= \frac{\phi(P)}{\pi h'} e^{i\pi n' (A_y + A_z) / \lambda} \sin \frac{\pi h'}{\lambda} (A_z - A_y). \end{aligned}$$

In order to apply this expression it is necessary to calculate the limits A_z and A_y of the numerical aperture corresponding to the diffraction maxima on the image side. It was shown in the previous paper that the measure of obliquity of the diffracted light was given by

$$m = \frac{\text{numerical aperture of the diffracted beam}}{\text{numerical aperture of the condenser}}.$$

Let x' be the interval in the final image plane corresponding to the interval x in the object plane; the optical sine relation gives

$$xA_\theta = x'A'_\theta,$$

* All the expressions used will now contain the wave-length if at all as λ , the wave-length in a medium of unit refractive index. The suffix o will be omitted from this point.

where A_θ is the numerical aperture of the converging beam corresponding to the numerical aperture A_θ of the diffracted light. The limits of the r th-order maximum are from

$$m + s_r = +1 \text{ to } m + s_r = -1,$$

i.e.
$$\frac{A_\theta}{A_0} + \frac{2\pi r}{v} = +1 \text{ to } \frac{A_\theta}{A_0} + \frac{2\pi r}{v} = -1,$$

or
$$A_\theta = (\lambda v / 2\pi x) (1 - 2\pi r / v) \text{ to } A_\theta = -(\lambda v / 2\pi x) (1 + 2\pi r / v).$$

Hence the limits for integration are

$$A_x = (\lambda v / 2\pi x') (1 - 2\pi r / v) \text{ to } A_y = -(\lambda v / 2\pi x') (1 + 2\pi r / v),$$

so that
$$A_x + A_y = -2\lambda r / x', \text{ and } A_x - A_y = \lambda v / \pi x'.$$

The amplitude and phase ϕ (P) corresponding to the r th-order term of the series

$$(\pi / v) (1^* + \sum e^{is_r u^*})$$

are π / v and $2\pi r u / v$.

This term therefore corresponds to a displacement represented by

$$\text{disp}_r = \frac{1}{h'v} \sin \frac{h'v}{x'} e^{2ir\gamma},$$

where

$$\gamma = \pi \left(\frac{u}{v} - \frac{h'}{x'} \right).$$

The full series then becomes

$$\begin{aligned} \text{disp} &= \frac{1}{h'v} \sin \frac{h'v}{x'} [1 + e^{2i\gamma} - e^{-2i\gamma} + \dots], \\ &= \frac{1}{h'v} \sin \frac{h'v}{x'} [1 + 2 \cos 2\gamma + 2 \cos 4\gamma + \dots]. \end{aligned}$$

Since the spacing x' of the geometrical image elements is proportional to the distance (l' , say) of the image from the posterior principal focus, i.e.

$$x' = l' / K,$$

where K is a constant, the expression above can be written in the form

$$\text{disp} = \frac{K}{l'} \cdot \frac{\sin (h'v/x')}{(h'v/x')} \{1 + 2 \cos 2\gamma + \text{etc.}\}.$$

This expression is similar to the one obtained previously on page 203 of the original paper, but it can be more readily interpreted. When an indefinitely great number of terms are included, it is a discontinuous function having zero values except at points defined by the conditions

$$\gamma = 0, \text{ or } \pm \pi, \text{ or } \pm 2\pi, \text{ etc.},$$

i.e. where
$$h' = x' (u/v), \text{ or } h' = x' (u/v) \pm x', \text{ or etc.}$$

When a smaller number of terms are taken, the separation of the main maxima (see below on next page) is also x' ; the similarity between object and image increases as more and more diffraction maxima come into action. Note that x' is the spacing prescribed by the optical sine relation for the case in question.

The maximum found where $h' = x'u/v$ corresponds to the aperture lying at the point defined by the phase angle u . As h is the distance in the object plane corresponding to the distance of this aperture from the centre of the illuminating concentration given by the condenser, the value of u is

$$u = 2\pi h A_o / \lambda.$$

Since $v = (2\pi x A_o / \lambda)$ we have

$$h' = h (x'/x).$$

It is therefore seen that if we move the illuminating disc the images will remain stationary in the same positions. Hence the positions will be constant for a multiplicity of illuminating points, i.e. for a source of finite size.

In order to study the effect of varying the position of the illuminating point in respect to the object, it is more convenient now to take a reference point fixed with respect to the grating; let it be some one aperture, and let the relative position of the maximum of illumination in the object plane be expressed (in terms of phase as above) by u_1 . The grating space (in terms of phase) is v as before. Thus the phase interval corresponding to the first aperture beyond the illumination point will be $v - u_1$. Hence we may put $v - u_1$ in place of u in the foregoing work.

Further, the displacement denoted by h' in the image is one measured from the centre of the spherical reference surface corresponding to the illumination point, so that if displacements in the image plane are now to be measured from the new reference point corresponding to the selected aperture above, and a distance so measured is H ,

$$h' = H - x' (u_1/v),$$

since the displacement of the image point corresponding to the central maximum must be $x' (u_1/v)$.

On making these substitutions γ becomes $\pi (1 - H/x')$ and the final series above becomes

$$\text{disp} = l'^{-1} \{ (Hv/x') - u_1 \}^{-1} K \sin \{ (Hv/x') - u_1 \} \{ 1 + 2 \cos 2\pi (1 - H/x') + 2 \cos 4\pi (1 - H/x') + \text{etc.} \},$$

which, if an infinite number of terms are included, has zero values except where

$$2\pi (1 - H/x') = 0, \pm 2\pi, \pm 4\pi, \text{ etc.},$$

i.e. where

$$H = \pm x', 0, \pm 2x', \text{ etc.}$$

As in the previous paper, the intensity is shown as proportional to the square of the amplitude.

$$\text{Intensity} \propto \text{Amplitude}^2 = K^2 l'^{-2} \{ (Hv/x') - u_1 \}^{-2} \sin^2 \{ (Hv/x') - u_1 \} \{ \text{cosine series} \}^2.$$

The intensity corresponding to a finite extension of the source of light will be found by integrating this expression between values of u_1 corresponding to the range of the image of the source projected by the condenser. An imaginary source of infinite extent will give an intensity proportional to

$$\frac{K^2}{l'^2} \{ \text{cosine series} \}^2 \int_{-\infty}^{+\infty} \frac{\sin^2 (V - u_1)}{(V - u_1)^2} du_1,$$

where V is written for Hv/x' . The value of the integral part is π , so that the intensity is proportional to

$$(\pi K^2/l'^2) \{1 + 2 \cos 2\pi (1 - H/x') + \text{etc.}\}^2,$$

and the intensities of all the image points would be equal.

Similar conclusions apply to the positions of the maxima in the interferences shown when only the central and the two first-order diffraction maxima produce the interference effects in the region of the image plane. In that case the amplitude variation is represented by the terms

$$1 + 2 \cos 2\pi (1 - H/x'),$$

and has main maxima of amplitude 3, where

$$H = 0, \pm x', \pm 2x', \text{etc.},$$

and secondary maxima of amplitude -1 , where

$$H = \frac{x'}{2}, \frac{3x'}{2}, \frac{5x'}{2}, \text{etc.}$$

The corresponding intensities are 9 and 1. The positions of these maxima will be constant for all illuminating points in a source of finite size.

§ 3. CASE OF DARK-GROUND ILLUMINATION

We may consider the case of dark-ground illumination as a reduction form of the case above. The light from the central maximum fails to reach the image, and the effects may in a likely case be due to symmetrical parts of the two first-order maxima, the second-order lying outside the aperture range of the objective. It is instructive first to consider this condition in detail. The limits of numerical aperture occupied by the first-order maxima on one side are

$$\{(\pi/p) - A_1\} \quad \text{and} \quad \{(\pi/p) - A_2\},$$

where A_1 and A_2 are the limiting numerical apertures of the dark-ground illuminator. (That is unless some parts of *these* maxima happen to fall outside the range of the objective, a condition which would need separate consideration.) In the present instance, the amplitude is found by taking the integration over the limits

$$\pm \frac{x}{x'} \left(A_1 - \frac{\pi}{p} \right) = \pm \frac{A_1 x - \lambda}{x'},$$

and

$$\pm \frac{x}{x'} \left(A_2 - \frac{\pi}{p} \right) = \pm \frac{A_2 x - \lambda}{x'},$$

for the terms $r = \pm 1$. The resulting expression on writing

$$\alpha_1 = \frac{\pi h' (A_1 x - \lambda)}{\lambda x'}, \quad \alpha_2 = \frac{\pi h' (A_2 x - \lambda)}{\lambda x'}, \quad \beta = \frac{\pi u}{v},$$

is

$$(2ih'v)^{-1} [e^{2i\beta} (e^{2i\alpha_1} - e^{2i\alpha_2}) + e^{-2i\beta} (e^{-2i\alpha_1} - e^{-2i\alpha_2})],$$

or

$$2 (ih'v)^{-1} \sin (2\beta + \alpha_1 + \alpha_2) \sin (\alpha_2 - \alpha_1).$$

With the same substitutions as before, viz. $u = v - u_1$, $h' = H - x'u_1/v$, the expression becomes

$$\frac{2}{i(Hv - x'u_1)} \sin 2\pi \left\{ 1 - \frac{H}{x'} + \frac{x}{2\lambda} \left(\frac{H}{x'} - \frac{u_1}{v} \right) (A_1 + A_2) \right\} \sin \pi \left\{ \frac{x}{\lambda} \left(\frac{H}{x'} - \frac{u_1}{v} \right) (A_2 - A_1) \right\}.$$

It is to be remembered that this expression only relates so far to the case of a single illuminating point. The extreme factors represent a broad amplitude-variation of the $U^{-1} \sin U$ type, in which the spacing of the bands would depend on $A_2 - A_1$, and would become broader as $A_2 - A_1$ diminishes numerically.

The remaining factor is of such a form that the value of H giving the maximum value of the sine term must depend on u_1 , i.e. on the relative location of the central point of illumination in the object plane. Hence any multiplicity of illuminating points would be bound to yield a set of non-coincident maxima, and as we must in practice always use a source of light having finite dimensions, the interferences will not be visible in ordinary practice. They could not be seen in any case unless the range of the illuminating points were small in comparison with the object spacing.

The next case for consideration is that in which the aperture range of the objective is great enough to allow both first- and second-order maxima to take effect, the direct-light maximum of zero order still being screened. The presence of the second order is represented by adding the appropriate term to the above expression. The numerical-aperture range of the second-order maximum on one side is

$$\{(2\pi/p) - A_2\} \text{ to } \{(2\pi/p) - A_1\}.$$

The second-order term for one side will therefore be

$$(2ivh)^{-1} e^{4i\beta} (e^{2i\alpha_1'} - e^{2i\alpha_2'})$$

in addition to the corresponding first-order term

$$(2ivh)^{-1} e^{2i\beta} (e^{2i\alpha_1} - e^{2i\alpha_2}),$$

where

$$\alpha_1' = \frac{\pi h' (A_1 x - 2\lambda)}{\lambda x'},$$

$$\alpha_2' = \frac{\pi h' (A_2 x - 2\lambda)}{\lambda x'}.$$

When symmetrical dark-ground illumination is employed there will be in addition the corresponding terms obtained from the above by changing the signs of all the exponential terms in the two brackets. Adding the two expressions set out above we obtain

$$(2ivh')^{-1} e^{2i\beta} (e^{2i\alpha_1} - e^{2i\alpha_2}) (1 + e^{2i\gamma}),$$

as might have been found at once from the general formula of page 239. This can be expressed in the form

$$(vh')^{-1} e^{i(2\beta + \alpha_1 + \alpha_2)} (1 + e^{2i\gamma}) \sin(\alpha_1 - \alpha_2),$$

or

$$2(vh')^{-1} e^{i(2\beta + \gamma + \alpha_1 + \alpha_2)} \sin(\alpha_1 - \alpha_2) \cos \gamma.$$

When the illumination is symmetrical the combined result is clearly

$$4(ivh')^{-1} \sin(2\beta + \gamma + \alpha_1 + \alpha_2) \sin(\alpha_2 - \alpha_1) \cos \gamma,$$

or, written in full,

$$4 (ivh')^{-1} \sin \left\{ 3\pi \left(\frac{u}{v} - \frac{h'}{x'} \right) + \frac{\pi h' x}{\lambda x'} (A_1 + A_2) \right\} \sin \frac{\pi h' x}{\lambda x'} (A_1 - A_2) \cos \pi \left(\frac{u}{v} - \frac{h'}{x'} \right).$$

On substitution for u and h' as before, the first sine term becomes

$$\sin \left\{ 3\pi \left(1 - \frac{H}{x'} \right) + \frac{\pi x}{\lambda} (A_1 + A_2) \left(\frac{H}{x'} - \frac{u_1}{v} \right) \right\},$$

and this clearly has its maxima at values of H depending on u_1 . The same statement applies also to the second sine term, but *not* to the cosine term. Hence the effects of the cosine maxima will be cumulative as the dimensions of the source of illumination are increased, and these maxima occur at consecutive values of H differing by x' as shown above, so that they correspond to the intervals of the geometrical image points.

When further diffraction maxima come into action, the expression in the symmetrical case may be written

$$\begin{aligned} & (vh')^{-1} \sin (\alpha_1 - \alpha_2) [e^{i(2\beta + \alpha_1 + \alpha_2)} \{1 + e^{2i\gamma} + e^{4i\gamma} + \text{etc.}\} \\ & \quad - e^{-i(2\beta + \alpha_1 + \alpha_2)} \{1 + e^{-2i\gamma} + e^{-4i\gamma} + \text{etc.}\}], \\ & = 2 (ivh')^{-1} \sin (\alpha_2 - \alpha_1) [\sin \delta + \sin (\delta + 2\gamma) + \sin (\delta + 4\gamma) + \text{etc.}], \end{aligned}$$

where

$$\delta = 2\beta + \alpha_1 + \alpha_2.$$

On expanding the sine brackets, the expression can be written

$$\begin{aligned} & 2 (ivh')^{-1} \sin (\alpha_2 - \alpha_1) [\sin \delta (1 + \cos 2\gamma + \cos 4\gamma + \text{etc.}) \\ & \quad + \cos \delta (\sin 2\gamma + \sin 4\gamma + \text{etc.})]. \end{aligned}$$

The number of terms to be taken in the cosine and sine series depends on the number of diffraction maxima which can contribute their effects. The case in which the first and second orders above are present has been dealt with above. If a considerable number are acting, the cosine series tends to give small values except at the points representing the geometrical image points, as has been shown, but the effect of the sine series is not cumulative in the same way, and its effect is negligible in comparison with that of the cosine series. Thus as the additional maxima come into play, there would be a closer and closer approximation to a series of extremely localized images representing the series of indefinitely small apertures constituting the object.

There is no need to extend the above treatment to the case of a series of apertures of finite width, since there is no doubt that the conclusions would be very similar.

It is therefore clear that the first-order maxima cannot by themselves produce interference phenomena representing the geometrical image in any exact sense, and that it is only when maxima of different orders are allowed to act more or less in entirety that the interferences in a definite surface bear a geometrical relation to the object.

The treatment of this subject on the lines of the Abbe principle (following up the

work begun by Cross) will not be given here. The essential features of the discussion would follow lines very similar to those used in the theory of bright-ground images. It would be found that the interferences due to pairs or groups of homologous maxima would agree only in the geometrical image. In dark-ground illumination the direct beams, on either side of the normal, would be considered independently; this seemed to the writer to be a matter requiring closer examination, but the results of this paper, so far as they go, constitute a justification of the theoretical applicability of the Abbe principle. Of course the conditions assumed in the theory are greatly modified in practice. It is not claimed that the use of a symmetrical dark-ground illuminator does always produce an accurately focused image of the light-source in the object plane. The argument is rather that even if this were the case, the necessity of considering the interference phenomena in image-formation cannot be avoided. It seems worth while again to point out that when the object consists of a transparent structure, the interference effects on which we rely to produce a picture can only be made effective by a deliberate restriction of the apertures of illumination and observation, with a consequent uncertainty as to the precise geometrical configuration of the object.

§ 4. PRACTICAL TESTS

In order to gain some experience of actual effects with an object of known character under dark-ground illumination, a few trials have been carried out with a set of Grayson's test-rulings. The specimen, kindly supplied by Sir Thomas Lyle, contained a series of bands ruled in a realgar film. The rulings are protected by a cover-glass, and there is presumably a film of water or some other medium between the rulings and the cover-glass to allow of the passage of light at numerical apertures greater than unity. The bands consist of a few lines at 5000, 10,000, 15,000, and so on up to 60,000 lines to the inch.

The objective was an excellent 16-mm. apochromat by Beck; the full numerical aperture was 0.35, but it could be limited to 0.18, if required, by means of a diaphragm placed near the posterior focus. The eye-piece used for visual trials was a $\times 20$ compensating.

The illumination was produced by a 100-c.-p. pointolite arc placed at the focus of an achromatic auxiliary condenser which projected a parallel beam into the substage condenser of the microscope. This was a well-made condenser of the Abbe type with an iris diaphragm; it was fitted with three special diaphragms having annular apertures corresponding to the following measured ranges of numerical aperture: 0.25 to 0.34; 0.375 to 0.45; 0.6 to 0.7. The centering of the illumination received due care.

Visual tests showed that the objective worked well at the normal tube-length; the system is not very sensitive to changes of tube-length at low numerical aperture.

A series of photographs was taken as follows, after some preliminary trials to ascertain correct exposures.

Set A. Objective numerical aperture = 0.18. Blue filter, Wratten No. 45 used throughout.

1. Bright-ground illumination. Full cone (condenser aperture 0.18). Illuminant focused in object plane.
2. Same conditions as in 1, but illuminant no longer in focus. Objective aperture still filled with light.
3. Dark-ground stop no. 1. Illuminant in focus.
4. Dark-ground stop no. 2. Illuminant in focus.
5. Dark-ground stop no. 3. Illuminant in focus.

Set B. Objective numerical aperture = 0.35.

1. Bright-ground illumination. Full cone (condenser aperture 0.36). Image of illuminant in focus. Blue filter.
2. Dark-ground stop no. 2. Illuminant in focus. Blue filter.
3. Dark-ground stop no. 2. Illuminant in focus. Red filter, Wratten No. 1. Panchromatic plate used for photography.

Examination of the plates gave for set A the results shown in table 1.

Table 1

Set A

	Objective numerical aperture	Illumination numerical aperture	Notes
1	0.18	0.18 Bright ground	Bands resolved up to 15,000. None higher
2	"		Same as with no. 1
3	"	0.25 to 0.34 Dark ground	Bands resolved up to 10,000. None higher
4	"	0.375 to 0.45 Dark ground	Bands resolved up to 15,000
5	"	0.6 to 0.7 Dark ground	Bands resolved up to 20,000

The above results are largely in accordance with the predictions of elementary theory*; it will be noticed that the introduction of dark-ground illumination gives a smaller resolving-power than with bright-ground until the numerical aperture of the dark-ground illumination is practically three times that of the objective. In the case of no. 5, where the dark-ground illumination has a numerical aperture still higher, the images of the 15,000 and 20,000 bands no longer consist of equally spaced parallel lines, but have a somewhat irregular spacing. The correct number of

* See L. C. Martin, *An Introduction to Applied Optics*, 2, 127 (Pitman, 1932). Elementary theory indicates that if the higher limiting aperture A_t of the dark-ground illumination is only slightly greater than that of the objective with aperture A_0 , the minimum grating-interval that can be resolved is little better than λ/A_0 , i.e. the interval must be about double that resolvable by the same objective with bright-ground illumination. As the aperture of the dark-ground illumination increases, the minimum interval resolvable is $2\lambda/(A_0 + A_t)$, so that when $A_t = 3A_0$ the minimum interval resolvable is about $\lambda/2A_0$; the performance in this respect is then as good as can be obtained with the same objective with bright-ground illumination. The best that can be expected of an apochromatic objective in numbers of lines per inch visually resolvable is approximately 10^6 times the numerical aperture. Thus at 0.18 we may hope to resolve 18,000 lines per inch, and so on.

lines, as shown by bright-ground photographs, appear, but the irregularity seems to be due to a diffraction phenomenon of the nature of an end effect.

The results for set B are shown in table 2.

Table 2

Set B

	Numerical aperture of objective	Numerical aperture of illumination	Notes
1	0.35	0.36 Bright ground	Bands partly resolved at 35,000. None higher
2	"	0.375 to 0.45 Dark ground, Blue light	Lines of some kind visible both in 30,000 and 35,000 bands, but 25,000 band not well resolved. 20,000 well resolved
3	"	0.375 to 0.45* Dark ground, Red light	Lines of some kind visible up to 30,000. None higher

In this set of photographs it was a surprise to find an apparent resolution of the lines in the 30,000 and 35,000 bands, seemingly in contradiction to the predictions of theory. It would not be expected that the 35,000 band would be resolved unless the aperture of the dark-ground illumination were increased to a value exceeding unity in the present case. The resolution is less marked with red light, but is, at first sight, still in excess of expectation†.

The relative spacing of the lines seemed to be so much in accord with what might be expected from the known frequencies, that the appearances were actually mistaken for real images until the plates were measured, with the results shown in table 3. There are slight differences of magnification between the plates, but the numbers in the rows should nearly agree if genuine images are produced.

The spurious lines are diffraction fringes associated with the edge effects at the sides of the bands. Their frequency is evidently dependent on the angle of diffraction of the first-order maximum, and hence there is a very deceptive variation roughly corresponding with the frequency of the actual rulings.

In order further to elucidate the conditions arising in the above cases, an examination of the diffraction maxima in the posterior focal surface of the objective was carried out; first for the condition obtaining for plate B 2. Each band of rulings produces its own set of diffraction maxima; hence a Ramsden eye-piece was employed and a slit diaphragm was placed in its focal plane in the microscope so as to expose the image of one band at a time. The corresponding diffraction maxima could then be observed in the exit pupil of the eye-piece without interference from those of other bands. The results are indicated in figure 7.

* As the condenser is non-achromatic, the actual numerical apertures obtained with blue and with red light may differ slightly.

† Enlargements of the negatives were prepared with a view to reproduction, but it was found that the detail would in all probability be lost in printing and the project was abandoned.

Table 3. Mean Interval (arbitrary units)

Band	Plate B ₁ Bright ground, blue	Plate B ₂ Dark ground, blue	Plate B ₃ Dark ground, red	Plate C ₁ Dark ground unilateral, blue
15,000	Out of focus	0.981 G 9 lines (distinct)	1.003 G 9 lines (distinct)	0.975 G 9 lines (distinct)
20,000 11 lines	0.756 G 11 lines (distinct)	0.736 G 11 lines (distinct)	0.937 S Not more than 9 lines visible (indistinct)	0.744 G 11 lines (fairly distinct)
25,000 14 lines	0.602 G 14 lines (distinct)	0.783 S Only 10 lines (some indistinct)	0.694 S Only 12 lines (indistinct)	0.701 S (Only distinct over part of band)
30,000 17 lines	0.470 G 17 lines (distinct)	0.610 S Not more than 13 lines (some indistinct)	0.593 S (Only distinct over part of band)	0.567 S Not more than 14 lines visible
35,000 19 lines	0.433 G 19 lines (faint)	0.508 S (Lines visible only over half the band)	(No lines visible)	0.504 S (Lines visible only over part of band)

G indicates a genuine image.

S indicates a spurious image.

The maxima would, if the objective were large enough, be complete rings, of which only limited parts are exposed in practice. Figure 8 is intended to indicate the approximate distribution of the complete maxima in the case of the 20,000 band, for blue light.

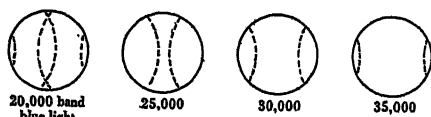


Figure 7.

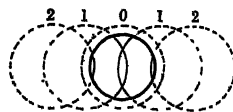


Figure 8.

With a greater number of lines, or with a greater wave-length, the distance between the maxima increases and the second-order maxima are no longer included within the objective aperture. Resolution can therefore no longer be obtained with dark-ground conditions.

Since it seemed possible that the presence of two first-order maxima might be responsible for some spurious fringes at least, a photograph was made with unilateral dark-ground illumination, so that only one first-order maximum should be exposed. In order to do this the annular aperture of the dark-ground diaphragm was closed except for a segment at one extremity of a diameter perpendicular to the lines. Blue light was used, and the results of this plate, C₁, are given in table 3. The results were much the same as before with the symmetrical illumination of the same numerical aperture, except that the spurious fringes are markedly one-sided.

It must not be inferred from this that symmetrical illumination is not superior to unilateral illumination in ordinary microscopy. The resolution of rulings is a very special case.

Using the 20,000 band alone, photographs were made of the exit pupil with unilateral illumination, both in blue light and in red light, figure 9. It will be noticed that there are secondary maxima present in both cases, but with the red there is only one main maximum, the first-order, present, as against both first and second-order maxima with the blue. This then is in accordance with the well-known criterion for distinguishing between real and spurious resolutions.

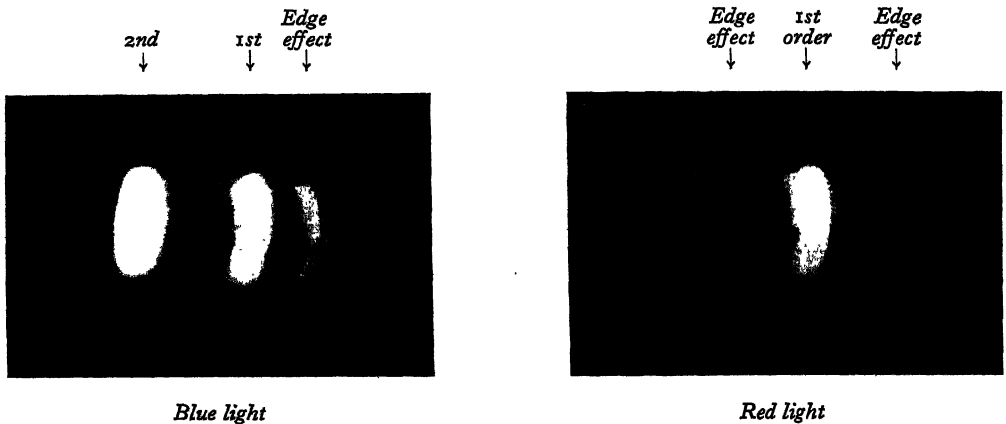


Figure 9. The exit pupil of the microscope with one-sided dark-ground illumination on the 20,000 band

The effects of the secondary maxima, which must be fairly prominent when the ruling consists of a few lines only, are well worth investigation, and the theory of the edge effects has not been investigated, so far as the writer's knowledge goes. It is therefore hoped to deal with these problems in the near future, as they are of considerable practical importance in the interpretation of the image in the microscope.

Finally it is not pretended that the above discussion or experiments convey an adequate account of the *general* question of the trustworthiness of the image in dark-ground illumination; nevertheless the theoretical and practical enquiries must start with the simplest possible cases. This paper should, however, convey a needed note of warning, as claims have been made that symmetrical dark-ground illumination is adequate to realize in every case the full resolving power of the objective. These claims cannot be theoretically substantiated. On the other hand the method of dark-ground observation may, by increase of contrast, reveal objects and structures which cannot be observed in any other way.

DISCUSSION

Mr T. SMITH. We should all agree with the author that an adequate theoretical discussion of microscopic imagery presents very great difficulties. Even the limitation to two dimensions of itself introduces some troubles of a formal nature. Another difficulty is to know how far we may apply results obtained, as in the present paper, by assuming that the numerical aperture is small. By way of illustration of these difficulties we may propound the question whether the ordinary expression for the numerical aperture is universally applicable, so that for instance any two portions into which a sphere is divided by a plane necessarily have the same numerical aperture, and in particular, whether the numerical aperture of a complete sphere is zero, and whether we must include among "small" apertures a nearly complete sphere.

Putting on one side the troubles connected with the range over which it is permissible to apply the theory in its present state, the difficulties which remain are by no means slight. In order to obtain results which may be stated in definite terms, it becomes necessary to sum the series which present themselves to infinity, and in so doing to assume conditions which depart to some extent from those which represent the actual problem. For we cannot of course in fact pass through a microscope objective light proceeding in a given direction from each of a very great number of parallel apertures. Perhaps it may be possible to show that when any considerable number of terms is taken the results will not differ very significantly from those corresponding to an infinite number of terms: if this were done it would add much to the strength of the arguments used. As things are I am inclined to agree with the author's conclusions for small apertures rather because they are in general concordance with my expectations than because the theory shows that in practice these conclusions must hold. If these theoretical difficulties can be surmounted I am sure the result will repay the labour involved. At the moment I believe that the most direct way to resolve at least one of the problems which the author has in mind would be to apply the experimental process he has described in his fourth section to the particular cases in which it is thought that exactly corresponding results have been obtained with dark- and with bright-ground illumination. To be of value the dark-ground conditions would have to be precisely those which are claimed to give these results, and therefore they must be set up by those who make these claims, and the counts and measurements made without disturbing these conditions. The bright-ground conditions present of course an altogether simpler question, and need occasion no difficulty.

I should be glad if the author could see his way to adding a fuller explanation to figures 7 and 8, as I am a little puzzled by the circles with unidirectional illumination of a plane grating. Also it would be of interest if he recorded on p. 231 what he includes in referring to the Abbe principle, since he clearly implies more than a treatment which starts out in the way described in the last ten lines of p. 233.

It will be clear from these comments that I think there is still needed a great deal of work, both theoretical and experimental, before we can understand the

high-aperture microscope and its limitations fully. The subject is unquestionably of great difficulty, and we should all feel grateful for any attempts that are made to add to our understanding and to face these difficulties openly. At the risk perhaps of appearing unduly critical, I have pointed to some difficulties which I think deserve attention in this paper, and I shall personally feel very grateful to Dr Martin if he can now or on some future occasion present the argument in a form which removes them. In any event I am sure his paper will be read and welcomed by those who are interested in microscopy and optical instruments generally.

AUTHOR'S reply. It is by no means easy to determine how far the results of an elementary two-dimensional discussion can be applied in practice, yet it seems fair to conclude that similar methods of analysis could be applied, and, as Mr Smith remarks, the fact that the elementary theoretical results are in harmony with actual observations should support the view that we are somewhat nearer an adequate theoretical approach than was previously the case. If I understand the matter rightly, the scope of the present treatment should cover a wider range of numerical apertures than would be comprehended in a purely paraxial type of case.

It is quite true that in dealing with the problem of the row of apertures the analysis can only be carried through to an algebraical solution by assuming an infinite number of apertures. Let us, however, consider a typical microscopical case in which some object with, say, 30,000 lines or dots per inch is being examined with an 8-mm. microscope objective of numerical aperture 0.65. The front lens of such an objective will have a fairly large actual diameter (approaching 1 cm. in some cases) and the field of a medium-power eye-piece may include a 1-mm. range of the object. It is therefore by no means unfair to assume that we have at least a thousand apertures all of which can contribute to the first-order and second-order maxima at the back of the objective. This represents, in our case, *five hundred terms* of a series like

$$\sin x + \frac{1}{3} \sin 3x + \frac{1}{5} \sin 5x + \text{etc.},$$

and it does not require a great deal of argument to see that the sum to infinity is a close approximation to the result. The expression near the foot of p. 237,

$$(\pi/v) (1^* + \sum e^{i\phi_s u^*}),$$

depends on an approximation of the same order. Even Mr Smith has sometimes been satisfied by fewer terms than five hundred in some aberration series! I know, of course, that this one is only slowly convergent, relatively speaking.

In another case I obtain the expression for the amplitude in the final image (near the foot of p. 239) as a series in which the successive cosine terms represent the successive diffraction maxima, and we can calculate the result of two, three, or more terms as more maxima are included in the range of numerical apertures. The sum to infinity is mentioned to imply that the distribution of light in the image only approximates closely to that of the object when a relatively great numerical aperture is allowed; it is not a step in the course of the argument.

With regard to figures 7 and 8, it will be remembered that the aperture of the dark-ground illuminator is restricted to a fairly narrow annular ring, and I have

tried to show the positions of the corresponding annular diffraction maxima by broken-line circles. The thick circle in figure 8 represents the limit of the objective, and circle o suggests the diffraction maximum of zero order (the direct light); circles 1 and 2 suggest the first-order and second-order maxima on each side. Thus figure 8 explains the case on the extreme left of figure 7. If the diffraction is effected by rulings of greater and greater frequency the second-order maxima pass quite out of the field, and leave the first order only, as is suggested in the successive parts of figure 7. In the case of the use of one-sided illumination, a segment of the annular aperture of the illuminator is exposed, and the corresponding diffraction maxima are similarly segmental.

I am also asked what is included in the Abbe principle? I understand it to mean the analysis of the method of image formation by the discussion of the diffraction of plane wave-trains at the object; it is usually assumed that the actual illumination can be resolved into groups of plane wave-trains incident at various angles. The mathematical foundations of this assumption have been examined by Dr Johnstone Stoney* and the applications of the principle have been worked out in papers too numerous to mention, but grave doubts have been felt as to whether the principle is valid in conditions of critical illumination.

I feel fairly confident that the principle is definitely applicable in the case of the type of object assumed in this theory, i.e. apertures regularly spaced in a thin opaque screen. On the other hand, we have the assurance of distinguished microscopists like Mr Conrad Beck that he has obtained resolutions in dark-ground illumination, when observing regular structures like diatoms, which are beyond the predictions of theory, and Mr J. Smiles tells me that he and Mr Barnard have been able to photograph images giving more than the theoretical resolution even when the diminished wave-length is taken into the theoretical account in dark-ground illumination with an ultra-violet dark-ground illuminator. I agree with Mr Smith that some such trials as he suggests might well be made, because if these claims were justified in practice it would point to some special physical explanation such as the partial decoherence of the light vibrations produced by the elements of the structure, or to the necessity of confessing that the ordinary methods of analysis are hopelessly at fault in the problem of resolution by high powers.

Mr Smith's problems about the numerical aperture of a complete sphere, etc., do not seem to arise in ordinary microscopical practice, in which we deal with objects illuminated by transmitted light alone, or by reflected light alone. Image formation due to both reflected and transmitted light would have to be analysed with respect to the two actions, and the numerical aperture in either case could not exceed the value of the relevant refractive index. I do not see that there is any difficulty arising through such questions in the present connection.

Finally I should like to thank Mr Smith for his criticism and for some suggestions, communicated privately, which have helped me considerably to improve the formal presentation of some mathematical parts of the paper.

* *Phil. Mag.* October, November and December, 1896.

ON THE USE OF CHARCOAL IN MAINTAINING HIGH VACUA

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ABSTRACT. Measurements have been made of the limiting pressures reached by charcoals and silica gels cooled with liquid air or liquid hydrogen when a small, constant stream of gas is admitted into the apparatus.

§ 1. INTRODUCTION

IN experimental work it is often essential to maintain a low pressure in a metal box with waxed joints. Since the metal is continually giving off gas, the box must be continuously evacuated and this is usually done with a mercury or oil condensation pump connected to the box by as short a length of wide tube as is practicable. The use of these pumps very often gives trouble, since it is impossible to avoid severe vibration of the apparatus, nor is it always convenient to place a fast pump sufficiently near the apparatus to be exhausted:

It is the purpose of these experiments to find out to what extent the older method of using cooled charcoal can be employed to maintain a low pressure in a vessel continually giving off small quantities of gas. Although many measurements have been made⁽¹⁾ on the limiting pressures reached by well-exhausted charcoals and liquid air when sufficient time is allowed for complete absorption, very few determinations appear to have been made on the equilibrium pressures reached when a constant stream of gas is introduced into a vessel containing cooled charcoal.

In the experiments to be described the pressures were measured with an ionization gauge. This type of gauge was chosen because it is simple to make and can be made to read the lowest pressures. The chief disadvantage of this type of gauge, namely, that it is difficult to degas sufficiently, was in these measurements an advantage, the hot metal of the gauge being used as the supply of gas of composition suitable for the experiment.

The following materials were used as absorbers: commercial silica gel; a special silica gel, completely freed from adsorbed salts by prolonged dialysis⁽²⁾; birchwood charcoal*; gas-mask charcoal Rb I†; Norit AK T II†; charcoal G 1000†; specially prepared charcoal used by Dr Lambert.

The experimental procedure was to place the charcoal or gel in a wide vertical glass tube with a side piece leading through a wide-bore tap to the pumping system.

* Obtained from Messrs Hopkins and Williams, London.

† Samples of these charcoals were kindly presented by the British Carbo Union, Ltd.

The ionization gauge was attached vertically above the charcoal by means of a large ground joint lubricated with Shell Apiezon L grease of negligible vapour pressure. Before the charcoal was introduced into the apparatus it was roughly evacuated with an oil pump, while the silica gel was heated in an open silica dish over a large Meker burner. After this treatment a weighed quantity (about 8 gm.) was introduced through a funnel into the vertical tube, and maintained at from 350 to 400° C. with the pump running until the evolution of gas became very slow; this usually took about 3 hours. No attempt was made to remove the last traces of gas by prolonged evacuation.

§ 2. PRESSURE-MEASUREMENT

Two series of experiments were carried out. In the first a 2-stage mercury condensation pump was used to evacuate the system, and the ionization gauge consisted of a cylindrical anode 1 cm. in diameter, a concentric spiral grid 0.4 cm. in diameter, and a central filament. Under working conditions the anode voltage was 1000 V., the anode current 6 mA. and the grid voltages - 20 to - 30 V. The filament current was supplied by a small transformer and the grid current was measured with a reflecting galvanometer.

The measure of the pressure in such a gauge is the ratio R of grid current to plate current. It is easy to calculate approximately, from the dimensions of the gauge, the numerical factor connecting the measured quantity R with the pressure.

The electrons in passing from the filament to the plate are accelerated from rest to 1000 V., producing a certain number of positive ions by collision with the gas in the gauge. These are collected by the negative grid, and constitute the grid current. Now it is known experimentally⁽³⁾ that a 1000-volt electron on being brought to rest in air at 1 mm. pressure, has a path of 5 cm. and produces 21 positive ions. Thus, if p is the pressure in the gauge in mm. of mercury, $R = \frac{21}{5} \times \frac{1}{2}p$, or $p = \frac{1}{2}R$ approximately.

Since this gauge was not sufficiently sensitive to measure the lowest pressures reached, for the second series of experiments another gauge was made up consisting of a fine wire anode between two flat plates to collect the positive ions. This arrangement of the electrodes produces a more sensitive gauge, since the electrons circulate several times round the wire anode and so have a longer path in the gas. A suitable gauge is described by Jaycox and Weinhardt⁽⁴⁾, who have also calibrated it against a McLeod gauge. The same calibration was used.

§ 3. EXPERIMENTAL RESULTS

Series I. The volume of the apparatus was 190 cm³; the whole was baked out and the rate of rise of pressure due to gas coming from the gauge was measured. As the mean of six readings the pressure rose from $1.2 \cdot 10^{-4}$ to $1.1 \cdot 10^{-3}$ mm. in 40 seconds, corresponding to 475 cm³ of gas per second at 10^{-5} mm.

On connecting to the pump the pressure fell to $1.1 \cdot 10^{-4}$ mm., corresponding to a pumping speed of 43 cm³/sec. This was in good agreement with Knudsen's

formula for the resistance of a tube system, according to which the maximum possible speed was $80 \text{ cm}^3/\text{sec}$.

Table 1. Series I

Adsorbent material	Observations
Commercial silica gel	When the residual gases were removed by the pump, the pressure fell to $3.1 \cdot 10^{-5} \text{ mm.}$, and on disconnection of the pump rose at first quickly and then slowly to about $2 \cdot 10^{-4} \text{ mm.}$, after which it rose very slowly at about $1.5 \cdot 10^{-6} \text{ mm. per minute}$ for an indefinite period
Specially purified silica gel	With the tap turned to the pump, the pressure fell to $2.2 \cdot 10^{-5} \text{ mm.}$, and on disconnection of the pump the pressure rose steadily for about 10 minutes to $4.8 \cdot 10^{-5} \text{ mm.}$ and then remained constant
Dr Lambert's charcoal	With the tap turned to the pump, the pressure fell to $8.5 \cdot 10^{-6} \text{ mm.}$, and on disconnection of the pump the pressure of the residual gas rose steadily at $7 \cdot 10^{-6} \text{ mm. per minute}$

Table 1 shows that the purified gel is much better than the commercial gel, especially for absorbing the residual gases (probably hydrogen), but cannot be used to replace charcoal if pressures lower than $5 \cdot 10^{-5} \text{ mm.}$ are wanted.

A comparison of the initial rate of accumulation of non-absorbed gas with the measured speed of the pump showed that for the silica gels the lowest pressure reached was determined by the vapour pressure of the absorbed gas.

Series II. The volume of the apparatus was 820 cm^3 , and the rate of evolution of gas was $172 \text{ cm}^3/\text{sec.}$ at 10^{-5} mm. When the gauge was exhausted by the pump alone the pressure fell to $1.9 \cdot 10^{-5} \text{ mm.}$, corresponding to a pumping speed of $90 \text{ cm}^3/\text{sec.}$

Table 2. Series II

Adsorbent material	Observations
Dr Lambert's charcoal	With both pump and charcoal the pressure fell to $4.7 \cdot 10^{-6} \text{ mm.}$, and on disconnection of the pump only rose slightly, reaching a constant value of $7 \cdot 10^{-6} \text{ mm.}$ in 5 minutes
Rb I	The lowest pressure reached was $3.3 \cdot 10^{-5} \text{ mm.}$ (i.e. higher than with the pump alone), and on disconnection of the pump the pressure rose steadily and indefinitely
Norit AK T II	This charcoal gave off relatively small quantities of gas on evacuation but formed a small white sublimate on baking. The behaviour was very similar to that of Rb I
G 1000	This gave a limiting pressure on the pump of $1.4 \cdot 10^{-5} \text{ mm.}$, but on disconnection of the pump the pressure rose steadily at about $4 \cdot 10^{-6} \text{ mm. per minute}$
Birchwood charcoal	The lowest pressure was $3.3 \cdot 10^{-6} \text{ mm.}$, and the residual gas produced a rise of only $5 \cdot 10^{-7} \text{ mm. per minute}$

The birchwood charcoal was also cooled with liquid hydrogen. The pressure fell to $5.5 \cdot 10^{-7}$ mm. and remained at this low value as long as the liquid hydrogen lasted—about 15 minutes.

§ 4. DISCUSSION OF RESULTS

A comparison of the two results for Dr Lambert's charcoal, in which the pressures were measured by independent gauges on different specimens, shows remarkably good agreement. The ratio of the rates of evolution of gas in the two experiments was $2.7 : 1$, while the ratio of the pressures as measured on the two gauges was $1.8 : 1$.

The experiments show that the charcoals specially prepared to have large absorptive power at room temperatures do not give satisfactory results under vacuum conditions. Even with the best charcoals the pressure rises slowly owing to the accumulation of unabsorbed gas, so that if the low pressure has to be maintained for several hours it is essential to use a pump.

The most effective procedure is to cool the exhausted charcoal with liquid hydrogen. Since the rate of evolution of gas in the gauge has been measured and the dimensions of the tube connecting the gauge to the cooled charcoal are known (length 20 cm., diameter 1.8 cm.), one can calculate the chance that a molecule of gas will be reflected on hitting the cool surface. If this is zero so that every molecule hitting the charcoal is absorbed, the calculated pressure in the gauge is $5.0 \cdot 10^{-7}$ mm., a result which is in excellent agreement with the observed value of $5.5 \cdot 10^{-7}$ mm. Thus a surface of charcoal cooled with liquid hydrogen approaches the theoretically perfect absorbing material.

§ 5. ACKNOWLEDGMENT

In conclusion I have to thank Prof. F. A. Lindemann, F.R.S., for extending to me the facilities of his laboratory, and for his kind interest in the work.

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THE ILLUMINATION-RESPONSE CHARACTERISTICS OF VACUUM PHOTOELECTRIC CELLS OF THE ELSTER-GEITEL TYPE

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ABSTRACT. The authors deal with the present status of the vacuum photocell as regards proportionality of photoelectric current to incident illumination, and give a series of observations which show that, while excellent cells are obtainable, their employment for precise work without a previous test is unsafe. A theory is developed which accounts for the observed results and gives over a limited range an equation of the form $S = K_1 + K_2/\sqrt{E}$, where S is the cell-sensitivity and E the illumination. Attention is called to the dependence of the illumination characteristic upon the colour of the light employed. The bearing of the theory on the application of Talbot's law to non-linear photocells is discussed.

§ 1. INTRODUCTION

THE relation between photoelectric current and incident illumination has been the subject of a large proportion of the investigations dealing with the photoelectric effect, though the point of view from which the question has been approached has changed progressively with lapse of years. Early in the history of the subject the natural point of view was the academic one having as its object the explanation of the mechanism of the photoelectric effect. Later, with increasing realization of the possibilities of the photoelectric cell as a photometer, the practical aspect has slowly superseded the academic and it has become a matter of importance to know to what extent a given cell may depart from the ideal as regards proportionality of photoelectric current to illumination.

The classical papers by Elster and Geitel⁽¹⁾, Lenard⁽²⁾, Griffith⁽³⁾, Richtmyer⁽⁴⁾, and Ives⁽⁵⁾ describe most of the methods available for investigating the illumination-response curve, and bring to light many of the difficulties associated with precise measurements on these lines. They establish the law of proportionality in the general physical sense over very wide ranges of illumination, and many subsequent papers^(6, 7, 8, 9, 10, 11) confirm this result for both vacuum and gas-filled cells, though in the case of the latter it was soon recognized that too high a *gas amplification*, as it is now termed, introduced measurable deviations from linearity of response^(5, 12, 13, 9, 14, 15). Long-period fatigue effects became apparent under

these conditions^(14, 15) and affected the validity of the measurements. Finally a short-period effect, with influence on the performance of gas-filled cells under flickered illumination^(16, 17, 18), was also found. The primary electron-emission has, however, been found to commence and terminate simultaneously with the incident illumination⁽¹⁹⁾. Among other factors affecting the shape of the response curve there are to be noted electrode-disposition and the presence of more or less isolated films of metal in the cell^(12, 5, 32).

To sum up, the above-mentioned researches leave little doubt as to the proportionality of photoelectric current to illumination under ideal conditions, and give considerable insight into the various difficulties encountered in attaining strict proportionality in practice. As a result it is now possible to obtain vacuum cells in which the approximation to strict proportionality is close enough for ordinary photometric purposes, but this fact does not dispose of the necessity for carefully testing a cell intended for precision photometry. The troubles likely to be met with in the application of the photocell to accurate photometry have been summarized in papers by Ives⁽²⁰⁾, Gibson⁽²¹⁾, Harrison⁽²²⁾, Ives and Kingsbury⁽²³⁾, and Winch⁽²⁴⁾, and in a paper recently submitted to the *Illuminating Engineer* by the present authors.

In view of the importance of the subject of linearity of response the authors have therefore carried out the tests described in the present paper with the objects (i) of assessing the usefulness of certain cells for commercial photometric work and (ii) of utilizing the results obtained for a more detailed study of the reasons for non-linearity, and of its bearing on the use of the photocell for heterochromatic photometry. The paper is limited to cells of the vacuum type, which are the only ones now used for precise measurements.

§ 2. EXPERIMENTAL METHODS

Experimental methods of investigating photocell illumination characteristics differ chiefly in the ways in which the known changes in illumination are produced. These include the application of the inverse-square law and of Beer's law, the addition of several light-sources, and the use of crossed Nicol prisms. The use of crossed Nicol prisms is attended by several difficulties and is open to the objection that polarization effects may be introduced, although some investigators have claimed high accuracy for the method⁽¹⁾. Mathematically, the inverse-square law is equally sound provided that the usual precautions as to size of source and so on are taken. It is, however, necessary to employ a diffusing window in front of the photocell, or alternatively to place the cell inside an integrator illuminated through an aperture by the light-source, and either of these arrangements introduces some uncertainty as to the true illumination values. The validity of the results depends on the attainment of perfect diffusion by the window, or of a uniform coating on the interior of the integrator. Again, the use of filters with monochromatic illumination, and the application of Beer's law of absorption⁽²⁾ are inapplicable if the photocell response curve obeys the relation found by Steinke⁽⁹⁾, because in this case the departure of the response curve from linearity appears only as a change in the

exponent in Beer's relation⁽¹⁰⁾. The absolute value of this exponent is seldom known with sufficient accuracy for small deviations from the accepted value to be laid to the charge of the photoelectric measurements. The additive method, used by Elster and Geitel in 1893⁽¹¹⁾ and dealt with again more fully by Campbell⁽²⁵⁾, remains the most suitable method and was used for all the work described in the tables given in the present paper. (The electrometer apparatus shown in figure 1 and described hereafter served only to draw attention to the influence of colour on the observed results.)

Among sources of error on the electrical side it is perhaps well to mention one which has frequently been overlooked; that is, that when the photocell is included in circuit with a high resistance and a constant source of e.m.f. the voltage on the cell will depend on the current flowing in the circuit^(26, 27, 28).

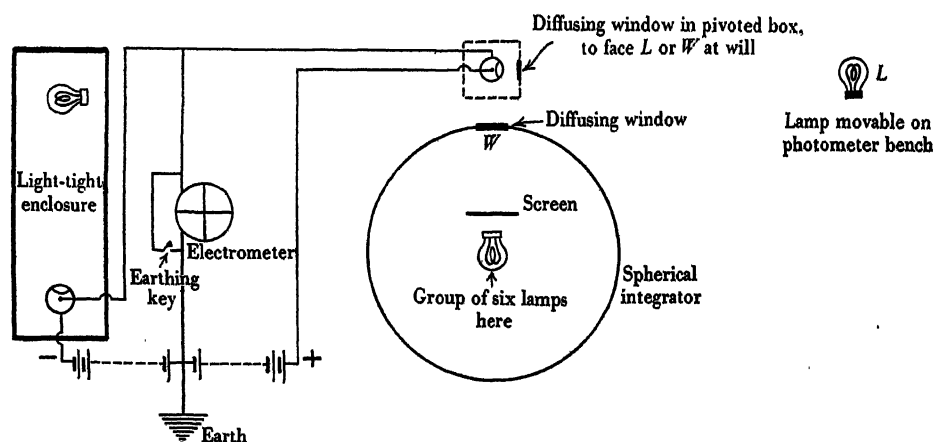


Figure 1.

§ 3. DESCRIPTION OF APPARATUS

For direct measurements of response curves a thermionic bridge photometer was used^(29, 24), the photocell, grid resistance and associated valve being enclosed in an earthed screening-box while the rest of the apparatus was unscreened. The photometric system was similar to the sphere and associated photocell in the figure. The sources of light were enclosed in an integrating sphere of diameter 1 m. and consisted of six 100-V., 30-W. vacuum lamps made specially to ensure uniformity of rating, constancy of light output, and good repetition performance. The photocell received light from a small diffusing-window in the integrating sphere. The six lamps were mounted on a common baseboard and separately wired to a junction system outside the integrator. Any lamp or group of lamps could be connected thus to a pair of $\frac{1}{2}$ -inch-square copper bus-bars by means of stout copper bridges inserted into mercury cups. A constant voltage was maintained on the bus-bars during a set of observations. Thus it was possible to increase the illumination on the photocell in steps by switching in the lamps one at a time. The observed value of photoelectric current for any group of lamps alight together was then compared

with the figure obtained by adding readings for individual lamps lit separately, and so the deviations from linearity of response could be noted. The object of using lamps of uniform rating was not simply to attain equal steps of illumination (these were not to be expected, if only on account of the different positions of the lamps in the integrator) but to ensure that light of one colour should be used. This precaution was shown to be justified by work on the variation of colour response with light-intensity, an effect which had been pointed out previously⁽²³⁾.

It was in the case of a photometer of the null type that the authors noticed the effect of change in the colour temperature of the source on the illumination response characteristic of the cell. The photocell could be illuminated either with light direct from a lamp on a photometer bench, or by means of the window of an integrating sphere containing a comparison lamp. In ordinary photometry the photocurrents under these two conditions are made equal by adjusting the position of the lamp on the bench. Equality is assured by balancing the current against a constant current from a second independent photocell, an electrometer being used as a null instrument. This photometer is called the *electrometer photometer* hereafter, and is shown diagrammatically in figure 1.

§ 4. PRELIMINARY RESULTS

Tests with the thermionic bridge photometer soon showed that for some photocells, at least, evidence of non-linearity was apparent and that in nearly every case the sensitivity of the cell diminished as the illumination was increased. The deviations from linearity were not generally so great as those quoted by Carruthers and Harrison⁽³⁰⁾ in their investigation on Talbot's law, but were of the same sign. It thus remained to eliminate the possible sources of error in the apparatus before attempting further precise results.

Another phenomenon was however noticed in using the electrometer photometer (figure 1). In order to investigate whether the diffusing window of the cell-box in this photometer were satisfactory it was decided to utilize the bank of six lamps already available. These were placed in the integrating sphere instead of the usual comparison lamp. They were lit singly and in groups, and the corresponding distances of the bench lamp to give the same photocurrents were observed. If these distances were $d_1, d_2, \dots, d_6, d_{1-2}, d_{1-3}, d_{1-4}$, etc., then on the assumption that equality of photocurrent denotes a definite proportionality between sphere illumination and bench illumination, the colour of the sources remaining unchanged throughout, we should have

$$\frac{1}{d_{1-2}^2} = \frac{1}{d_1^2} + \frac{1}{d_2^2},$$

$$\frac{1}{d_{1-3}^2} = \frac{1}{d_1^2} + \frac{1}{d_2^2} + \frac{1}{d_3^2} \text{ and so on,}$$

provided that the diffusing window were satisfactory and that its surface might justifiably be taken as the bench origin. It was soon found, however, that the equations were not precisely obeyed and, further, that the diffusing window was not

the cause of the discrepancies, since other experimental conditions changed the magnitude and even the sign of the error. The factor having the greatest influence appeared to be the colour difference between sphere lamps and bench lamp. Accordingly the experiments were repeated with various colour differences, the balance of illumination being maintained for the same lamps run at different voltages by means of stops on the window of the integrator. The various bench distances were thus made very closely the same in every case, so that any influence of poor diffusion of cell-window would be the same for every set of measurements.

In a particular example in which the bench lamp was run at 65 V. the value of $\frac{1}{d_{1-6}^2} / \sum_{1-6} \frac{1}{d^2}$ was 0.988 when the sphere lamps were at 100 V., and 1.001 when the sphere lamps were at 65 V.

The repetition accuracy of the photometer was at least 0.1 per cent on a single reading, and two readings were taken on each lamp or group of lamps, so that the difference between the two ratios just given is a real one. It can be accounted for only by supposing that the sphere lamps interact with each other differently at different voltages, or that the departure of the photocell characteristic from linearity over the same range of photocurrents is different for light of different colours. The latter explanation proved to be correct, as is shown below. The cell used was the rubidium thin-film vacuum cell again mentioned below.

§ 5. TESTS ON THE THERMIONIC BRIDGE APPARATUS

Tests on the connections of the six lamps showed that each lamp was without influence electrically on the rest, the voltage-drop on the bus-bars with all lamps burning being much too small to cause an appreciable drop in the candle power of the set of lamps, as compared with the sum of individual candle powers. Tests were also made photometrically by covering four lamps with a light-tight box. No change in the candle power of the remaining two was detected on switching the others on and off. Repetition performance of the lamps and photometer together was found to be better than $\frac{1}{4}$ per cent in general.

This allows for changes in sensitivity of the cell, if any, and in several cases possible changes in transmission of coloured glasses with change in temperature. As a check on consistency, in the later work, every set of observations was repeated and in no case was the difference between the two sets sufficient to throw doubt on the validity of the results.

Tests on the thermionic bridge photometer circuits included tests on possible photosensitivity of the valve associated with the photocell and the usual examination for steadiness of zero. In addition the precaution was taken of selecting anode and grid resistances having a low temperature coefficient, so as to minimize drift. The value of grid resistance generally used was 50 megohms, higher values being avoided where possible in order to minimize leakage difficulties. With a sensitive bridge galvanometer and suitably scaled grid potentiometer the overall sensitivity was ample.

The following blank experiments were made to show that the observed non-linearity was really due to the photocell and not to the electrical circuit. (1) With the cell darkened, known potentials were applied to the valve grid circuit in the thermionic bridge by means of a carefully standardized potentiometer. The readings of the photometer were found to be strictly proportional to the applied potentials. (2) In order better to simulate experimental conditions, the photocell and the battery supplying it were replaced by a standard 100-megohm resistance and potentiometer (used to apply, as well as measure, potential). The photometer scale readings were again found to be proportional to the scale readings of the standard potentiometer to within about 0.05 per cent from full scale to one-tenth of full scale. (3) Finally, two photocells were taken, and their illumination response characteristics found by means of the thermionic bridge photometer. They were then connected together in opposition in the photometer so that the apparatus then measured the differential photocurrent. Further, a shutter over one cell was adjusted to make this differential current zero for any one of the bank of six equal lamps, and then fixed. A set of readings on two to six lamps then gave the difference in output between the two cells over this illumination range. It was found to be equal, within the limits of observational error, to the value deduced from the difference between the individually measured characteristics. Since this method is a null method for the detection of non-linearity so far as the thermionic bridge circuit and grid resistance are concerned, it eliminates uncertainty which might arise from poor insulation of the latter and demonstrates the validity of the non-linear characteristics as given by the photometer employed for this investigation.

It should be noted that the effect of any difference in wave-length characteristic between the two cells used in this test was guarded against by selecting accurately colour-matched lamps. The colour-matching was done with the actual two-cell circuit described, so that the errors in matching could not have been responsible for the observed quantities, which were well outside the range of repetition accuracy. Attention may also be drawn here to the error in colour-matching which may ensue from the use of the usual two-cell circuit if the lamps to be matched differ widely in output, and if the two cells have different illumination characteristics.

§ 6. TABLES OF RESULTS

The thermionic bridge circuits, tested as described above, were used to obtain the following sets of observations. The illumination range was in every case only about six to one. Higher ranges could be no doubt obtained by the use of more lamps. The main reason for using only six in the present investigation was the avoidance of undue drift in the photocell and of changes in the transmission through coloured filters due to temperature changes.

It is worthy of note, as Steinke points out⁽⁹⁾, that some investigations have covered a wide range of values of illumination by subdividing this range into shorter sections, each of which is related to the next by some independent photometric comparison. In this case the error in the photometric comparison is introduced once

for every section covered and, if large compared with the deviation of the cell from linearity of response, may render the extension of the illumination range valueless.

The tables of results given below are selected from the whole of the work done and are therefore dated to show chronological order. In addition, the tables are divided into three sections, dealing with (i) earlier preliminary measurements with white light only, (ii) later measurements with coloured light, and (iii) one exceptional case. In every case relative sensitivity on an arbitrary scale is tabulated against the number of lamps alight. The mean photocurrent for the six single lamps is indicated also.

The figure for relative sensitivity is obtained by dividing the photocurrent corresponding to a group of lamps by the sum of the currents for the individual lamps lit separately. For a linear cell it would therefore be unity in every case. The cells used were as follows. The cathode material is as stated, to the best of the authors' knowledge.

Osram KMV6, No. 12255. Potassium on copper thin film, central plate cathode. Excess potassium in base of cell.

Osram infra-red cell. Caesium on silver thin film. Central plate cathode.

Gramophone Co. cell. Rubidium on silver thin film. Cathode on bulb, central anode.

Osram KMV6, No. 21076. Potassium on silver thin film, central plate cathode. No excess potassium.

Osram KV6, No. 21460. Bulk potassium, central plate cathode.

Philips Type 3512. Cathode on bulb, metal not stated.

Philips Type 3515. Cathode on bulb, metal not stated.

Osram KMV6, No. R0018. Potassium on silver thin film, central plate cathode.

(i) *White light.* Results for Osram Vacuum cell of type KMV6, No. 12255 (old type). The presence of a quantity of potassium in bulk in this cell caused instability of both wave-length and illumination characteristics with lapse of time.

Set 1. Date 17. v. 1932.

Number of lamps	Relative sensitivity		
	Cell volts 58	Cell volts 136	Cell volts 294
1	Unity (0.01 μ A.)	Unity (0.01 μ A.)	Unity (0.01 μ A.)
2	0.994	0.995	0.999
3	0.989	0.992	0.995
4	0.986	0.990	0.992
5	0.984	0.988	0.997
6	0.983	0.985	0.997

Set 2. Date 14. xi. 1932.

Number of lamps	Relative sensitivity		
	Cell volts 12	Cell volts 22	Cell volts 62
1	Unity (0.007 μ A.)	Unity (0.007 μ A.)	Unity (0.007 μ A.)
2	0.995	0.994	0.994
3	0.992	0.991	0.990
4	0.991	0.989	0.987
5	0.990	0.987	0.985
6	0.989	0.986	0.984

Results for Osram infra-red cell.

Set 3. Date 24. v. 1932.

Set 4. Date 14. xi. 1932.

Number of lamps	Relative sensitivity cell volts 58	Relative sensitivity cell volts 22
1	Unity (0.0105 μ A.)	Unity (0.007 μ A.)
2	0.998	1.000
3	0.997	0.999
4	0.996	0.998
5	0.995	0.997
6	0.997	0.997

Results for Gramophone Co. cell.

Set 5. Date 17. v. 1932.

Set 6. Date 14. xi. 1932.

Number of lamps	Relative sensitivity cell volts 58	Relative sensitivity cell volts 22
1	Unity (0.0096 μ A.)	Unity (0.007 μ A.)
2	0.992	0.994
3	0.988	0.992
4	0.986	0.992
5	0.984	0.991
6	0.983	0.991

In addition to these results measurements were made on the KMV6, No. 12255 cell with and without the filter used for colour correction in ordinary photometry (a green liquid filter). There was some indication that the results were slightly different according as the filter was used or not.

(ii) *Coloured light.* The following results were obtained during July, 1933, on seven cells of different types, six of which were supplied as suitable for photometric purposes. Three colour-filters were used in conjunction with them to select different spectral ranges. The same range of photocurrents was used for different tests on the same cell, in order that the electrical conditions in the cell might be comparable in the different cases. This necessitated adjustment of the illumination in accordance with the relative colour sensitivity of the cell, since light of different colours was used. The cell-voltages were those recommended by the makers with the exception of the rubidium cell, which was tested at two voltages to determine

whether its spherical shape and large size were likely to lead to discrepancies due to non-attainment of saturation; and of the Philips cell of type 3515. This cell was probably gas-filled, as the results seem to indicate, and a voltage of 26 was arbitrarily assigned to it.

Furthermore, on the advice of manufacturers, the photocurrents were of smaller value than previously, so as to ensure definitely that the cells were not overloaded.

The coloured filters used consisted of Chance glasses. The blue cobalt glass had a transmission of 21 per cent at 4200 Å. falling to $1\frac{1}{2}$ per cent at 4800 Å. The green glass transmitted 34 per cent at 5400 Å., the value falling to 4 per cent at 6000 Å. and 4800 Å. The red selenium glass transmitted about 86 per cent from the infra-red to 6700 Å. and cut off sharply at a wave-length slightly shorter. The lamps were not operated at the same voltage in the case of each filter, but the voltage changes were always such as to emphasize the colour-changes imposed by the filters.

Set 7. Osram KMV6 cell No. 12255 at 22 V. Photocurrent for one lamp, 0.00101 μ A.

Number of lamps	Relative sensitivity with		
	Blue filter	Green filter	Red filter
1	Unity	Unity	Unity
2	0.999	0.989	0.998
3	0.995	0.981	0.997
4	0.994	0.976	0.997
5	0.993	0.972	0.995
6	0.991	0.966	0.994

Set 8. Osram KMV6 cell No. 21076 at 22 V. Photocurrent for one lamp, 0.0019 μ A.

Number of lamps	Relative sensitivity with		
	Blue filter	Green filter	Red filter
1	Unity	Unity	Unity
2	1.000	1.000	0.999
3	1.000	1.000	0.999
4	1.000	1.000	0.999
5	0.999	0.999	0.999
6	0.999	0.999	0.999

Set 9. Osram KV6 cell No. 21460 at 22 V. Photocurrent for one lamp, 0.00051 μ A.

Number of lamps	Relative sensitivity with		
	Blue filter	Green filter	Red filter
1	Unity	Unity	Readings unobtainable. Sensitivity too small
2	0.998	0.999	
3	0.997	0.999	
4	0.997	0.998	
5	0.997	0.998	
6	0.997	0.997	

Set 10. Osram infra-red cell at 22 V. Photocurrent for one lamp, $0.00085 \mu\text{A}$.

Number of lamps	Relative sensitivity with		
	Blue filter	Green filter	Red filter
1	Unity	Unity	Unity
2	0.998	1.000	1.000
3	0.994	1.000	1.001
4	0.992	0.999	1.001
5	0.990	0.999	1.001
6	0.988	0.999	1.001

Set 11. Gramophone Co. cell at 22 V. Photocurrent for one lamp, $0.0014 \mu\text{A}$.

Number of lamps	Relative sensitivity with		
	Blue filter	Green filter	Red filter
1	Unity	Unity	Unity
2	0.951	0.990	0.999
3	0.926	0.980	0.999
4	0.909	0.974	0.999
5	0.899	0.969	0.997
6	0.891	0.965	0.996

Set 12. Gramophone Co. cell at 138 V. Photocurrent for one lamp, $0.0015 \mu\text{A}$.

Number of lamps	Relative sensitivity with		
	Blue filter	Green filter	Red filter
1	Unity	Unity	Unity
2	0.966	0.989	0.998
3	0.940	0.985	0.998
4	0.920	0.980	0.999
5	0.901	0.977	0.999
6	0.893	0.974	0.999

Set 13. Philips cell, type 3512, at 22 V. Photocurrent for one lamp, $0.0012 \mu\text{A}$.

Number of lamps	Relative sensitivity with		
	Blue filter	Green filter	Red filter
1	Unity	Unity	Unity
2	0.938	0.985	1.000
3	0.904	0.973	0.996
4	0.880	0.967	0.994
5	0.861	0.960	0.993
6	0.848	0.957	0.990

Set 14. Philips cell, type 3515, at 26 V. Photocurrent for one lamp, $0.0014 \mu\text{A}$.

Number of lamps	Relative sensitivity with		
	Blue filter	Green filter	Red filter
1	Unity	Unity	Unity
2	0.927	1.001	1.008
3	0.894	1.001	1.014
4	0.873	0.999	1.016
5	0.860	0.998	1.017
6	0.850	0.997	1.018

The apparent rise in sensitivity for red light in the case of the Philips 3515 cell may be due to the gas-filling or to a rise in temperature affecting thermionic emission. The latter cause is improbable, however, since a repeat reading on one lamp immediately after one on the group of six lamps confirmed the previous reading on the same lamp. The presence of a small residuum of gas may account for the upward bend in the results of set 10.

(iii) Set 15. Date 11. x. 1933. Osram KMV6 cell No. R0018 at 22 V. Photocurrent for one lamp, $0.002 \mu\text{A}$. Tested with 100-volt lamps running at 53 V. No colour-filter.

Number of lamps	Relative sensitivity
1	Unity
2	1.000
3	0.998
4	0.997
5	0.995
6	0.995

In the case of set 15, the sensitivity corresponding to exposure to light from a group of lamps persisted for some little time after extinguishing the lamps, returning gradually to the original state for one lamp. No such prolonged change was observed in any other case, though tests were always made to detect it if possible. Set 15, therefore, is not explained by the theory given below.

§ 7. SUMMARY OF RESULTS

The above results show that in the employment of a photocell for precise photometry no assumption as to its linearity should be made. On the other hand they show that a carefully made modern cell may prove on test to be linear. Again, a cell may be linear for light of one colour and markedly non-linear for light of another colour. The bearing of this on photoelectric spectrophotometry is obvious. It implies too that curves of spectral sensitivity of a cell will depend on the illumination-values used for the calibration⁽²³⁾ and is in fact a sort of Purkyně effect, as was pointed out to the authors by Dr J. W. T. Walsh. The bearing of the effect on heterochromatic photometry in which photoelectric cells are used with a null method is perhaps not at first obvious, though it is exactly analogous to the similar case in visual photometry.

Suppose that $\phi_1(E_1)$ represents the photocurrent i for illumination E_1 of colour temperature T_1 and that $\phi_2(E_2)$ represents that for illumination E_2 of colour temperature T_2 ; then in a null method, we adjust E_1 and E_2 to give equal photocurrents, say i' . We then have

$$i' = \phi_1(E_1') = \phi_2(E_2').$$

If we make another setting at another value i'' of photocurrent (e.g. by bringing both sources closer to the cell) we have (say)

$$i'' = \phi_1(E_1'') = \phi_2(E_2''),$$

but since ϕ_1 and ϕ_2 are not the same function, we cannot deduce that

$$E_1'/E_2' = E_1''/E_2'',$$

which is the criterion for absence of the Purkyně effect.

The results described above and obtained with the electrometer photometer are thus explained by the fact that the rubidium cell used had distinctly different illumination characteristics for different regions of the spectrum (see set 11).

It is also noticeable that in almost every case the cell's sensitivity, if not constant, falls with increasing illumination. The few exceptions include one case of a cell (Philips 3515) which possibly was gas-filled and which in any case was of a type generally considered unsuitable on other counts for photometric purposes.

Finally it is clear that few cells have a response curve sufficiently near to the linear form to justify their employment, without the use of correction factors, in high-precision photometry to an accuracy of ± 0.1 per cent, except where the light-sources under comparison have very similar spectral distributions, and the cell is used at constant illumination. Where a cell is used for colorimetric or spectrophotometric purposes its illumination characteristic must be examined with light of the colour or colours for which it is to be used.

§ 8. POSSIBLE CAUSES OF NON-LINEARITY

In discussing the causes of non-linearity we may dismiss any effect of residual gas in the cell and confine attention to cells of modern manufacture in which the vacuum is hard enough to render such effects negligible. Earlier "vacuum" cells are less reliable in this respect.

Space-charge effects. Failure to attain saturation, due to space-charge effects, might be advanced as a possible cause. This is, however, discounted by the fact that the available evidence seems to show that the cell-sensitivity falls off less rapidly the higher the illumination, whereas space-charge effects become more serious. Again, results for blue and red light, as given above, were taken for the same range of photocurrent, and space-charge effects would presumably be the same in the two cases. The corresponding cell-characteristics are, however, often markedly different. On the other hand in some cases increase of cell-voltage appeared to improve the cell's performance, as would be expected if space-charge effects were in question.

Thermal effects. A second possible cause, namely drift due to heating of the cell by the incident radiation, is unlikely to have been operative during the recorded observations because, with the exception of the cell used for set 15, none of the cells tested showed evidence of such drift when exposed to the illumination from the six-lamp group for a period of time. Further, repetition of a single-lamp reading immediately after the six-lamp exposure showed no evidence of a change in cell-sensitivity due to the previous exposure to a higher illumination. It may also be noted that each complete set of observations took only ten minutes. Tests with a cupric chloride cell, absorbing the infra-red, also gave negative results on this point.

Effect of thin films of photoelectric material. It seems probable that the main cause of non-linearity is still the presence of films of photoelectric material in poor electric connection with the main cathode⁽³²⁾. These films may be on the glass walls, thus constituting a high resistance in themselves, or may perhaps be upon the surface of the cathode, but separated from it by a layer of a poorly conducting material. The latter formation is suggested at once by the method of preparation of many thin-film cells, in which the cathode plate is oxidized before deposition of the alkali metal. An oxide layer of the ideal thickness cannot probably be regarded as a semi-conductor, since it is of molecular dimensions (or of that order), but the presence of unavoidable thicker portions may provide ground for the supposition.

The photocurrent may then be supposed to come partly from a portion of the cathode in direct metallic connection with the cell terminal and giving a linear response, and partly from other portions or films in poor contact with the cell terminal. The potential-drop in the film due to the passage of the photocurrent will cause part of the film to reach such a voltage as to prevent electrons from escaping. The area of this part will vary with the photocurrent in the film, and so non-linear response will ensue. The overall characteristic of the cell will then be the sum of a linear characteristic and a non-linear one, due to different photosensitive areas in the cell. The change in characteristic with change in colour of the incident light then naturally follows from the fact that these areas have different spectral sensitivities due to their different structures and work functions.

An endeavour is made in the next section to develop the isolated-film hypothesis to account quantitatively for the observed results. Before proceeding to the theoretical considerations, however, we may note that the hypothesis gives a clear picture of the reason why the results of Carruthers and Harrison⁽³⁰⁾ show that non-linear cells obey Talbot's law. For if the illumination is flickered sufficiently rapidly, the current from the high resistance will take up an equilibrium value (probably not large enough to be detected during the period of occultation on Carruthers's oscillographs⁽³⁴⁾), owing to lag in leakage of charges developed by individual flashes of light. This is equivalent to the sort of "fatigue" suggested by Campbell⁽³³⁾, though he suggested temperature change as the cause. The cell will then of course behave in the same way as it would for a steady illumination of the same mean value. This will be so independently of the type of steady (illumination, response) function that may arise from the isolated-film hypothesis. Thus the equation given by

Stiles⁽³¹⁾ for the form of the illumination characteristic of cells obeying Talbot's law may not be unique, and in fact is not borne out by the observations already tabulated.

§ 9. THEORETICAL TREATMENT

Let AB represent a conducting photosensitive film of resistance R per unit length and connected at A with the cell cathode at potential P equal to P_0 . Suppose that at some point X in the film the potential P , equal to P_1 , is such that between A and X photoemission takes place while between X and B it is stopped. Such a precise line of demarcation will not in practice exist, but is here assumed in order to render a simple mathematical treatment possible. Consider a strip of the film, dl in length, distant l from X . Let the photoemission from it be di and the currents flowing in and out of the strip, as shown, be $i + di$ and i . Let the potential drop across the strip be dP . Let the incident illumination be E .

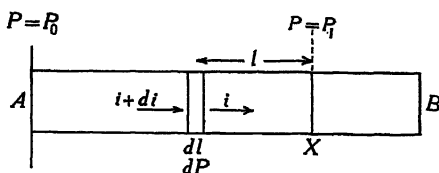


Figure 2.

Then we have

$$i = kEl \text{ where } k \text{ is a constant} \quad \dots\dots(1),$$

$$dP = iRdl$$

$$= kERldl \text{ by (1)}$$

and

$$P - P_1 = \frac{1}{2}kERl_0^2 \text{ by integration.}$$

Thus the total length l_0 of the photoelectrically active part of the strip is given by

$$P_0 - P_1 = \frac{1}{2}kERl_0^2,$$

and

$$l_0 = \sqrt{\left(\frac{2}{k} \cdot \frac{P_0 - P_1}{ER}\right)} \quad \dots\dots(2).$$

Now the total current from the strip $l_0 = kEl_0$

$$= \sqrt{\frac{2kE(P_0 - P_1)}{R}}.$$

Thus the illumination characteristic for the strip is of the form

$$\text{current} \propto \sqrt{\text{illumination}}$$

or

$$\text{sensitivity} = \frac{\text{current}}{\text{illumination}} \propto \frac{1}{\sqrt{\text{illumination}}}.$$

If now to complete the picture of the photocell we add a portion of cathode surface obeying a linear law, we obtain for S , the sensitivity or current \div illumination, an expression of the form

$$S = K_1 + K_2/\sqrt{E} \quad \dots\dots(3),$$

where K_1 and K_2 are constants, provided only that there remains some of the

strip AB which is inactive. Whether this is so or not will depend on the value assigned to P_0 , the value of R or the value of E .

The value of R cannot be controlled externally, but if P_0 or E is adjusted so that l_0 as given by equation (2) is greater than AB , the whole of the strip will be active and the cell will be linear. Again, for large values of E , the term K_2/\sqrt{E} in equation (3) will be small compared with K_1 and the characteristic of the cell will become more nearly linear, corresponding to a limiting sensitivity S equal to K_1 . The (sensitivity, illumination) curve will then consist of a short horizontal portion for small values of E , leading into a curve which falls somewhat abruptly at first, but which for higher values of E tends asymptotically toward a constant ordinate K_1 . This general shape, including the horizontal portion near $E = 0$, has been confirmed by work on one cell only over an extended range of illumination, but it is not desired to present incomplete and in some respects inconclusive evidence at the present juncture. Establishment of the illumination scale to the desired accuracy is difficult over the required range. Moreover the flat part of the curve did not in this case extend beyond the point corresponding to a photocurrent of about $0.0005 \mu A$. Measurements of both current and illumination below this point require considerable care.

In practice the assumptions as to the shape of the strip AB , and the existence of a line at X dividing the active from inactive portions of the strip, will not be fulfilled. But it is interesting to inquire whether the equation $S = K_1 + K_2/\sqrt{E}$ fits the observed values given earlier in this paper.

In the case of set 13 (blue filter) we have

S observed:	1.000	0.938	0.904	0.880	0.861	0.848
S calculated; $K_1 = 0.726$, $K_2 = 0.30$:	1.026	0.938	0.899	0.876	0.860	0.849

These calculated values show that if a good fit with observed values is obtained over the lower part of the curve, the upper observed value is low, as might be expected if the curve rounds off into a flat portion near $E = 0$. On the other hand a moderately good fit over the *whole* curve may be obtained with other values of K_1 and K_2 . The general shape indicated by the theoretical treatment is, however, borne out.

If we take set 11 (blue filter) even better agreement can be obtained, thus:

S observed:	1.000	0.951	0.926	0.909	0.899	0.891
S calculated; $K_1 = 0.810$, $K_2 = 0.20$:	1.010	0.951	0.926	0.910	0.899	0.892

The theory put forward above thus seems to fit the observed facts, but it is not claimed that the form of equation given is unique as regards agreement with practical results. Finally it must be emphasized that if the difficulties inherent in the use of a wider illumination-range can be satisfactorily overcome, extension of the results to such a range is most desirable.

§ 10. CONCLUSIONS

Measurements on a group of photocells of modern construction show that while cells are obtainable which give almost strict proportionality between photocurrent and illumination, it is unsafe to employ a cell for precise photometry without a linearity test. Moreover, since deviations from linearity may differ according to the colour of the incident light, calibration should, if necessary, be carried out at several different wave-lengths.

In almost every case the cell sensitivity falls with increasing illumination and may be expressed by an equation of the form $S = K_1 + K_2/\sqrt{E}$, which is developed upon the assumption that badly conducting photosensitive films present in the cell are responsible for non-linearity. This assumption is borne out also by the observed fact that deviations from linearity are greater the shorter the wave-length of light used, for the metallic film will probably have bulk-metal properties with maximum photosensitivity at shorter wave-lengths, while the main cathode contributing a linear quota of photocurrent will be of the oxide-layer type with maximum sensitivity toward longer wave-lengths.

The hypothesis of a poorly conducting film also explains the recorded fact that non-linear photocells obey Talbot's law, irrespective of whether the equation developed above is correct or not.

The resemblance of the non-linear properties of photocells to the Purkyně effect in the eye is mentioned, and the bearing of these upon heterochromatic photometry by null methods is pointed out.

§ 11. ACKNOWLEDGMENTS

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DISCUSSION

Dr J. W. T. WALSH. This paper settles at last the long-standing discussion as to whether the response of photoelectric cells can be taken as linear or not. It is clear that the assumption cannot be made and that cells must be tested for this property. The Research Laboratories of the General Electric Company showed at the Society's recent exhibition the apparatus used at Wembley for making this test and I hope Mr Winch will tell us more about their experience in this matter.

I should like to ask the authors whether they have found the sensitivity curves of cells to remain constant over extended periods either of use or of rest. Further, do they consider that, for work of the highest accuracy, no reliance should be placed on the linearity of the cells, if all measurements are made with the same value of the illumination? I hope they will continue their work and that, in particular, they will investigate more fully the form of the curve and especially the initial portion of it.

Mr G. T. WINCH referred to the substantial departure from linearity exhibited by the cell used in set 7 of the observations, as compared with the high degree of linearity shown in sets 8 and 9. This was possibly due to the fact that some of the excess potassium which is present in the older type of cell may have been deposited on the cathode as the result of very slight warming such as can occur through handling. The cells used in sets 8 and 9, being of much more recent manufacture, are not subject to this trouble. The speaker had tested several random-selected KMV6 cells with a developed technique and found that in three or four of them with light from tungsten vacuum lamps the departures from linearity did not exceed 5 parts in 10,000. It would be interesting to see the authors' individual measure-

ments; a comparison of the readings from set to set would indicate whether the claim for sensitivity was fully justified. It was surprising that sensitivity was shown always to decrease with increasing luminous intensity; the speaker had found small apparent fluctuations of sensitivity which he was inclined to think were as likely to be errors of measurement as changes in cell sensitivity, but he had not observed consistent unidirectional change with changing sensitivity.

Mr J. GUILD. The discrepancies discussed in the paper, are, of course, merely an example of what is always found when any physical phenomenon is utilized in apparatus intended for measurements of high accuracy: the apparatus never behaves in accordance with the simple laws which we are led to expect from the text-books or the academic investigations. In most of the earlier work on photoelectricity the emphasis has lain on the theoretical significance of the strict proportionality between intensity of illumination of any constant spectral energy-distribution and photoelectric emission as such. While we may have no present reason to doubt that this strict proportionality exists, it is necessary to bear in mind that our evidence for it is only its theoretical probability and not direct experimental confirmation, because any measurements we make must necessarily be made on the currents delivered not by a theoretically simple photosensitive surface but by a photoelectric cell complete with contact resistances, internal resistance and so on, which have long been suspected of producing disturbing effects of the kind the authors have here demonstrated. I think there is no doubt that the kind of schematic explanation of the departure from linearity given in the paper, though not necessarily the only possible one (as the authors admit), is substantially correct in its main features. I think also that the same underlying causes are responsible for the fatigue exhibited in very different degrees by different cells. I have not, myself, much direct acquaintance with the behaviour of vacuum cells, but I have made considerable use lately of various types of rectifier or photovoltaic cell. Some types of rectifier cell exhibit enormous fatigue effects, the current for a given illumination falling asymptotically to about a tenth of its initial value after 30 minutes' exposure or more, while other types show negligible or quite minute fatigue. While I have not examined these cells with exactly the same objects in view as the authors of the present paper, there seems to be a definite correlation between the magnitude of the fatigue effects and the departures from linearity of the (current, illumination) relation. This must not, of course, be confused with the departures from linearity due to external resistance in the galvanometer circuit, which all such cells exhibit and which is due to a different and well-known cause.

Without reference to underlying causes it is obvious that a cell which exhibits fatigue must also give a non-linear response, and, further that the departures from linearity will depend to some extent on the time sequence of the observations. Where the effect is marked, it should be appreciably different on the ascending and descending loops of a cyclic series of intensity-variations. I should like to know if the authors have found any such differences in the cells they have examined.

In reply to a question (asked later) by Dr Stiles, I do not know how accurately rectifier cells which exhibit marked fatigue obey Talbot's law, as I have not used sector discs with them except for quite rough purposes. I should say that they certainly obey it to within one or two per cent, but I have made no tests of greater precision.

As regards the practical aspects of the authors' results, they confirm the view that I and many others have always held, that when the highest quantitative accuracy is sought one should never rely on the assumed proportionality of response to stimulus, even with cells in which tests have failed to reveal a definite discrepancy, but should always adopt an experimental arrangement in which all the cell factors are eliminated. In work with *gas-filled* cells it is, in fact, desirable to ensure that the stimulation of the cell never alters during the whole of the processes involved in comparing two illuminations. If, for example, such a cell is exposed to one illumination, and is then left dark while a second illumination is brought to bear on it, it does not, in practice, follow that the second illumination is equal to the first when adjusted to bring the response of the cell to the same value. We have found it necessary, for substitution methods of this kind, to arrange matters so that a constant illumination falls on the cell during the complete process of substitution. The causes of difficulties of this kind may reside entirely in the gas, but they may possibly be in some part due to fatigue effects in the film, and I should be interested to hear if the authors have found any such effect with vacuum cells.

Dr W. S. STILES. The authors' explanation of the cause of non-linearity is of particular interest. The agreement of their experimental results with a derived law $S = K_1 + K_2/\sqrt{E}$ raises the question whether somewhat different assumptions as to the shape and other properties of the thin films would lead to the same result. The authors point out that their hypothesis would fit in with the obedience to Talbot's law of non-linear cells, because it gives a mechanism for a short-period fatigue in the cell's response. Some time ago I discussed the connection between non-linearity, fatigue and obedience to Talbot's law in photoelectric cells, and derived the formula $S = K_1 - K_2 E$ for the sensitivity⁽³¹⁾ assuming fatigue and recovery to obey a simple exponential law. The present accurate measurements show this result to be invalid, but there must still be a very close connection between the form of the fatigue curve and the shape of the response characteristic. A study of the fatigue curve, possibly by the method mentioned in my paper⁽³¹⁾, might lead to an estimate of the order of magnitude of the resistance and capacity of the thin film which are involved in the authors' theory.

Mr Guild mentioned the correlation he had observed between non-linearity and fatigue effects in various photovoltaic cells. It would be interesting to know whether the cells in question obey Talbot's law.

Mr G. P. BARNARD. I hope that the authors will regard equation (3) as an approach to a more general mathematical treatment. I do not feel that the theory

given in this paper for these cells can be directly applied, as has been suggested by Mr Guild, to the observed deviations from linearity in response of the Sperrschicht type of cell. An investigation at the National Physical Laboratory on the Sperrschicht cell is in progress; the results show definitely that other factors determine the form of the illumination-response characteristics. It is intended to publish shortly a paper on this work.

AUTHORS' reply. Dr Walsh has raised a question of perhaps greater importance than the simple consideration of linearity of response in asking whether the response curve remains the same for a particular cell over a period of time. For cells of the vacuum type containing no excess alkali-metal the answer is, fortunately, yes, so far as our experience is concerned. This is also a reply to Mr Winch's question as to the repetition accuracy of the quoted results. Several cells mentioned in the present paper showed consistent behaviour over a period of about a year. As regards the employment of photocells for photometry to an accuracy of ± 0.1 per cent, we consider that no assumptions as to linearity of response should be made. As Dr Walsh suggests, measurements should be carried out at constant illumination. Even then, colour differences are to be avoided where possible in order to exclude the type of Purkyně effect mentioned in the paper, which, however, generally involves errors of a smaller order than those arising from the employment of the cell for non-constant illumination. It is agreed that further work on the shape of the response curves is most desirable.

Mr Winch contrasts the results of set 7 with those of sets 8 and 9. We agree with his suggestion that the poorer performance in the former case may be due to the presence of free potassium which encourages the formation of stray films of metal. Mr Winch also stresses the systematic downward trend of the sensitivity curves we have measured, stating that his own observations had in general shown fluctuations in sensitivity above and below some selected normal value, as the illumination was increased. We would suggest that on *prima facie* physical considerations the former behaviour would seem the more probable. Moreover, the appearance of this systematic behaviour in our results is a strong argument in support of the claim that purely fortuitous error has been reduced to a very low order in the experimental work.

We cannot at the moment give a reply to Dr Stiles's question as to what laws of response would arise from the mathematical investigation of thin films of different shapes. In the case of the cells used by us the shape most likely to arise would be roughly rectangular. As Dr Stiles points out, there must be a close connection between the static response characteristic of a cell and its behaviour under flickered illumination. In fact the general argument advanced in his paper⁽³¹⁾ must clearly hold even if the present results indicate that some of his simplifications are not justifiable. Investigation of the average output of a cell at various frequencies of interruption of the light should certainly lead to further knowledge

concerning the resistance and capacity of the stray metal films. Alternatively we suggest observing by means of an oscillograph the form of the discharge from these films immediately upon the cutting off of a steady illumination.

Such cells of the rectifier type as have come to our notice have all shown obedience to Talbot's law for high frequencies of interruption. Mr Guild carries over the relation of fatigue and non-linearity to the case of the rectifier cell. While no doubt similar effects of metallic films occur here also, other factors certainly have an influence on the response characteristic of the cell, since in general it appears that the characteristic for a linear rectifier cell is a happy combination of a non-linear voltage curve with a non-linear resistance curve. In these respects we are indebted to Mr Barnard for information and look forward to seeing a fuller account of his recent work on this interesting type of photocell in the near future.

Reverting to the question of fatigue in general, it is convenient to distinguish between a short-period and a long-period fatigue without prejudice to the possibility of their being eventually ascribed to a common cause. Such fatigue as we have discussed already has been assumed to be of a period short compared with the time taken by the observations, though long compared with a single cycle of illumination in investigations on Talbot's law, for otherwise the law would not hold precisely⁽³¹⁾. There is sometimes observed, however, a long-period effect operative over periods upwards of several minutes. For instance the Osram cell No. Roor8 on further investigation showed a drop in sensitivity of over 1 per cent in 10 minutes under steady illumination, and a recovery in the dark at a corresponding rate, the curves being roughly of an exponential type. This was certainly not due to the cause which first suggested itself, namely temperature rise of the cathode, since the incidence of a beam of infra-red light (to which the cell was insensitive photoelectrically) was without effect. An alternative cause put forward by J. H. de Boer* seems more probable and has an interesting bearing on the suggestions made in the present paper.

* *Physica*, 18e, 9, 285 (1933).

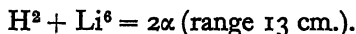
THE PREPARATION OF HEAVY HYDROGEN*

By P. HARTECK, PH.D.

Communicated by Prof. Lord Rutherford, December 7, 1933. Read December 15, 1933.

ABSTRACT. The method of working for the preparation of heavy hydrogen by means of the electrolysis of an alkaline solution with nickel electrodes is described in detail.

G. N. LEWIS and R. T. MACDONALD† have described the preparation of heavy hydrogen by means of the electrolysis of an alkaline solution with nickel electrodes. They do not give details of their experimental methods. There are, however, some precautions which must be observed if the enrichment of the heavy hydrogen (H^2) is to proceed satisfactorily. This paper gives a description of a convenient method of working. For working this out it was a great advantage that slightly enriched samples of water could be examined in the apparatus of Oliphant and Lord Rutherford‡ in which lithium is bombarded with hydrogen ions. The long range α -particles which are observed are due to collisions involving H^2 according to the equation



The amount of heavy hydrogen in ordinary water gives a measurable number of disintegration particles, and affords a rapid method of estimating the amount of H^2 at weak concentrations.

About 60 samples of enriched hydrogen, which had been prepared by electrolysis of normal water under varying experimental conditions, were tested in this way. When the method had been developed the H^2 concentration was determined by density-measurements. For the preparation of the highly concentrated samples of heavy water I started with water supplied by the Ohio Chemical Co. containing 0.33 per cent and 0.48 per cent of H^2 .

At the cost of power to the Cavendish Laboratory ($1\frac{1}{2}d.$ per kilowatt hour) it was uneconomical to make the initial stages of the electrolysis on the spot, and for that reason the enriched water was obtained for these experiments by Dr Cockcroft during his recent visit to the United States of America.

The electrolytic cells were made of nickel supplied by the Mond Nickel Co. The cells were soldered carefully on the outside so that practically no solder came in contact with the electrolyte. All metal parts which came into contact with the liquid or the condensed water of the cell were of nickel. Figure 1 shows a cell of capacity 5 litres. The cell is placed in a water bath and stands on legs which permit

* H. C. Urey, F. G. Brickwedde and G. M. Murphy, *Phys. Rev.* **39**, 164 (1932). E. R. Washburn and H. C. Urey, *Proc. Nat. Acad.* **18**, 496 (1932).

† G. N. Lewis and R. T. Macdonald, *J. Chem. Phys.* **1**, 341 (1933).

‡ M. L. E. Oliphant and Lord Rutherford, *Proc. R.S. A* **141**, 259 (1933). M. L. E. Oliphant, B. B. Kinsey and Lord Rutherford, *Proc. R.S. A* **141**, 722 (1933).

the circulation of water below the cell. Inside the cell there is a cooling-spiral of glass, not shown in the sketch. The case of the cell is the cathode, and the anode is a perforated sheet of nickel which can be adjusted to be exactly parallel to the bottom of the cell and a few millimetres above it.

The electrolysis is begun with $\frac{1}{2}$ per cent NaOH. With a current of 150 to 200 A.* and cooling-water at approximately 10°C . the temperature of the electrolyte does not rise above 25°C . In spite of the low concentration of NaOH the nickel of the anode does not go into solution because of the high current-density. The surface of the nickel is carefully cleaned before the electrolysis begins. Grease and organic compounds in general must be carefully avoided. The wet surface is scrubbed with glass paper and steel wool and the electrolysis is immediately begun. This

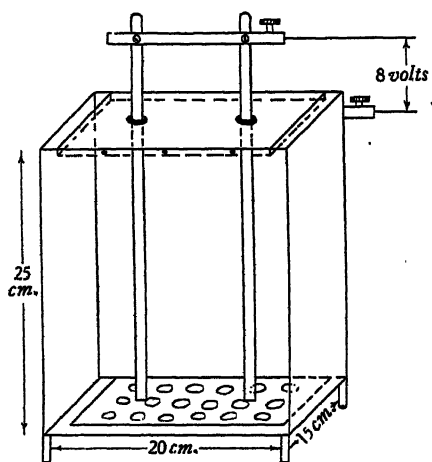


Figure 1.

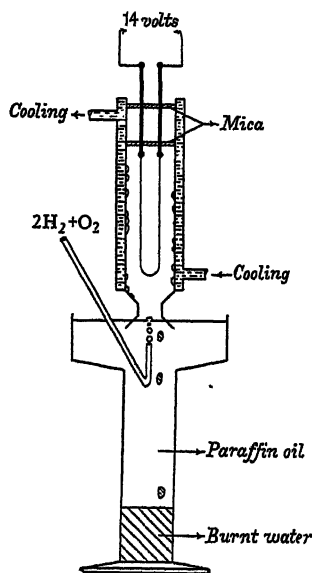


Figure 2.

method has been found to be more convenient than the addition during the electrolysis of a complex nickel salt which produces a new surface layer of nickel. If allowed to stand exposed to the air a nickel surface becomes coated with a layer of oxide which seems to lower the efficiency of the electrolysis. After the electrolysis of one or two lots of solution the surface is again cleaned. The sticks of NaOH are washed with distilled water before the solution is made up.

More than twenty-five electrolyses have been carried out in this manner with four different cells and without any case of failure. Since the initial concentration of alkali is so small, it is possible to electrolyse to $\frac{1}{20}$ or $\frac{1}{30}$ of the initial volume. The solution is then neutralized with CO_2 and the water is distilled off, as described by Lewis and Macdonald.

* Corresponding to a current-density of from 0.6 to 0.8 A./cm²

Let α and α' be the relative rates of removal by electrolysis for H^1 and H^2 . Then the amounts of residual H^1 and H^2 at time t are given by the equations

$$H_t^1 = H_0^1 e^{-\alpha t} \quad \text{and} \quad H_t^2 = H_0^2 e^{-\alpha' t}.$$

Lewis and Macdonald give a value $\alpha/\alpha' = 5$. In my last series of experiments α/α' was never less than 5.5 and was usually in the neighbourhood of 6.5. In calculating these values the effects of evaporation and losses during distillation were neglected. If corrections are made for these factors α/α' becomes slightly greater. No value of α/α' greater than 7 has been observed. The efficiency of the electrolysis seems to be independent of the concentration of alkali over a wide range. No definite increase of the efficiency was observed with increasing current-density provided this was greater than 0.6 A./cm². The dependence of the electrolysis on temperature was not investigated since it was always necessary to work at a low temperature to keep down evaporation.

If the electrodes are really clean the efficiency has its full value from the beginning.

Table. Efficiency of separation

No.	V_0 (cm ³)	V (cm ³)	$\frac{V_0}{V}$	H_0^2 (per cent)	H^2 (per cent)	$\frac{\alpha}{\alpha'}$
1	3000	300	10	0.33	2.3	6.7
4	3000	375	8	0.33	2.0	6.5
6	3000	100	30	0.33	5.3	6
10	110	6	18	12.5	90.0	5
15	40	1	40	12.2	100	—
23	2500	22.5	110	0.48	27	6
26	120	6	20	12	91.5	5.5

As soon as the concentration of H^2 had the value of about 12 per cent, the mixture of oxygen and hydrogen coming off from the cell was burnt to water to avoid loss.

The following method of working is efficient and safe. The gas mixture bubbles through paraffin oil in the bottom of a cylinder containing a white-hot platinum wire, figure 2. The top of the cylinder is made roughly air-tight with thin mica sheets. The gas mixture combines on the surface of the platinum wire. The water which is formed condenses on the water-cooled cylinder-wall and collects under the oil. Before this recovered water is used for further electrolysis it must be filtered to get rid of paraffin oil and distilled with 1 per cent $KMnO_4$.

The exact formula for the change of concentration of H^1 and H^2 at any value of the concentration of H^1 and H^2 is

$$\left(\frac{C_{H^1}}{C_{0H^1}}\right)^{\frac{\alpha}{1-\alpha}} \cdot \left(\frac{C_{0H^2}}{C_{H^2}}\right)^{\frac{1}{1-\alpha}} = \frac{V}{V_0},$$

where $\sigma = \frac{\alpha'}{\alpha}$ and is < 1 ; C_{0H^1} , C_{0H^2} and V_0 are the initial concentrations and volume, C_{H^1} , C_{H^2} and V are the corresponding quantities after the electrolysis. The equation is identical with that of Rayleigh deduced in the theory of fractional distillation. In figure 3 the ordinates are the logarithms of H^2 per cent and the abscissae logarithms of the ratio V_0/V . The curves represent the changing concentration of H^2 and H^1 as the volume diminishes for the two values $\frac{1}{5}$ and $\frac{1}{6}$ of σ ,

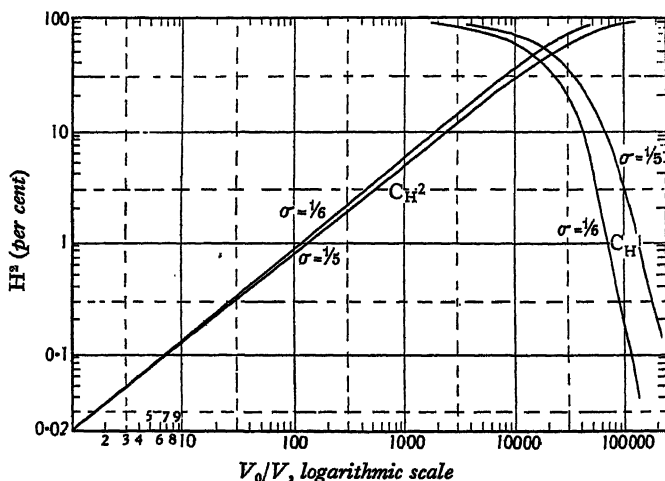


Figure 3.

corresponding to values 5 and 6 of α'/α . In this diagram it is assumed that α'/α remains constant over the whole range of concentration. This is certainly true as a first approximation—compare experiments 4 and 10 in the table.

In the course of these experiments we have obtained enriched samples of heavy water containing from 30 per cent to 98 per cent of heavy hydrogen, corresponding in all to about 25 cm³ of pure heavy water. Experience has shown that the 30-per-cent samples form a suitable source for obtaining supplies of heavy-hydrogen ions for transmutation experiments.

I am much indebted to Prof. Lord Rutherford and Dr Oliphant for their kind permission to test the concentration of H^2 with their disintegration apparatus, and to the Rockefeller Foundation for a grant.

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A HIGH-VACUUM LEAK DEVICE

By G. A. WHIPPLE, B.A.

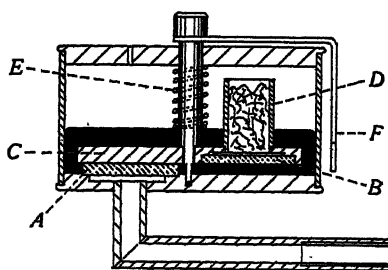
Communicated by Robert S. Whipple, December 13, 1933. Read in title, January 19, 1934.

ABSTRACT. The high-vacuum leak device described was designed for the control of pressure in the discharge tube of cold-cathode-ray oscillographs. It operates on a diffusion principle, and in this case permits of continuous variation of discharge-tube pressures from 0.5 mm. mercury to black vacuum at 70 kilovolts.

Other applications of a diffusion leak are indicated.

THE high-vacuum leak device described was designed for the regulation of the pressure in the discharge tube of cold-cathode high-voltage cathode-ray oscillographs. The discharge tube is continuously evacuated by a diffusion pump and air is admitted to it through some form of control valve or leak at such a rate as to maintain a pressure of about 1.2×10^{-2} mm. of mercury.

The leak described is based on a method used to admit small quantities of inert gas to small glass hot-cathode oscillographs. It relies for its operation on the diffusion of air through porous plugs whose porosity, whilst allowing free passage



to air, will not allow mercury to pass. A plug of this material, immersed in a cup of mercury, is connected to the apparatus under vacuum. If now a second porous plug is brought into contact with the first the mercury, owing to its high surface tension, is readily forced from between the two plugs and air is sucked through both plugs into the evacuated apparatus. The area of surface contact between the two plugs controls the rate of diffusion.

The construction finally adopted is shown in the figure. The porous plugs take the form of discs *A* and *B*, about 25 mm. in diameter. *A* is cemented into the bottom of a mercury container and is connected to the evacuated chamber. *B* is cemented flush into a rotor member *C*. A tube *D* admits air to the plug *B* and enables the rotor to be totally immersed in mercury, leaving the upper surface of *B* open to air at atmospheric pressure. It will be seen that when the rotor is in

the position shown the plug *A* is sealed by mercury. If the rotor is turned on its axis the two plugs will overlap; the extent by which they overlap governs the rate of diffusion, and is continuously variable. It was found advisable to make the rotor of polished rustless steel to avoid the rubbing of rust into the pores of *A*; and to plug the tube *D* with glass wool to trap grit and dust. The spring *E* serves to maintain the surfaces in contact. A pointer *F* is fitted to the rotor, and a reference scale may be attached to the container.

The magnitude of the leak can be varied by adopting different dimensions of, and materials for, the porous plugs. The plugs in use give a pressure-range from "black vacuum" to about 0.5 mm. of mercury with a discharge tube evacuated through an orifice of diameter approximately 10 mm. with a 4-stage mercury-vapour diffusion pump.

The leak can be adapted for the admission of gases to evacuated vessels by means of a double-plug rotor covering two plugs connected respectively to the gas container and to the vessel. Alternatively a flexible pipe connection may be taken to the tube *D*.

The thanks of the author are due to Mr W. L. Beck for suggesting the possibilities of a diffusion leak, and to the Cambridge Instrument Company Ltd. for permission to publish this note.

DISCUSSION

Prof. G. I. FINCH. The leak is stated to correspond to discharge-tube pressures between black vacuum and 0.5 mm. It seems to me that this is far too wide a range, especially since it is covered by a comparatively small angle of rotation of the lever. Such a leak is definitely unsuitable for electron-diffraction and also probably for cathode-ray oscillography, but it might be possible to narrow the range sufficiently by making the upper porous plug wedge-shaped with an acute leading angle.

AUTHOR'S reply. The point raised by Prof. Finch was fully appreciated in the initial stages of development. Two methods of solution presented themselves: firstly a vernier or slow-motion device for the rotor arm, and secondly a tapering plug design. Of the two, the second is admittedly the better device, but a moment's thought will show that unless the rotor is of large diameter and the plug is placed at its edge (which reduces the angle of rotation) the wedge must have curved edges, the line joining its apex to the mid-point of its base being struck about the centre of the rotor. The mechanical difficulties of this construction were considerable and were felt to be unnecessary, since leaks of the type described have now been in use, successfully, on high-speed cathode-ray oscillographs for the past few months. In this connection it should be added, however, that the oscillographs concerned employed a device, due to Prof. Finch, whereby the rate of evacuation of the discharge tube also may be continuously varied; thus the leak admitting air is not the sole means of controlling discharge-tube pressure.

THE IMAGE-DISTORTION AND OTHER EFFECTS DUE TO THE GLASS-THICKNESSES IN LENS SYSTEMS

By H. DENNIS TAYLOR

Communicated by the Taylor-Hobson Research Department, September 23, 1933.

Read December 1, 1933.

ABSTRACT. This paper discusses the optical influence upon distortion of image, or departures from correct pictorial representation, caused by the considerable thicknesses of glass involved in the construction of high-class photographic lenses or projectors of large angular field of view. Specific instances of such influence, and the appropriate formulae for expressing the amount of such distortion, are given.

FIGURE 1a represents a photographic twin lens construction L_1, L_2 whose first principal point is at P_1 and second principal point at P_2 . If χ is the angle which any point A_1 in the original flat picture to the left, as viewed from P_1 , makes with the optic axis XX , then freedom from distortion requires that the image of A_1 shall be formed at A_2 , so that $cA_2 = p_2c$ (the equivalent or conjugate focal length) multiplied by $\tan \chi$ exactly.

But if the image of A_1 falls at a_2 instead of at A_2 , then a_2A_2 is the linear radial displacement of the image, which in this case is towards the optic axis XX . Therefore a minus distortion is implied.

The usual method of expressing distortion is to state it in terms of R , which denotes the correct or first-order distance cA_2 from the lens axis XX , that is a_2A_2/R , or the linear displacement divided by $p_2c \tan \chi$. This is the fractional or percentage distortion, while a_2A_2 is the linear distortion.

It is well known that proportional distortion, of the second order, increases as R^2 or as $\tan^2 \chi$ and linear distortion as R^3 or as $\tan^3 \chi$.

In my book *A System of Applied Optics* I advocated a method of stating and computing the various aberrations of a thick lens by the device of treating it as if it were built up of two "elements" of vanishing thickness, the first e_1 being convexo- or concavo-plane and the second e_2 being plano-convex or plano-concave, while the two elements enclose between them a parallel plate of the same glass and of a thickness t equal to the axial thickness of the solid lens. In accordance with this device the two elements e_1 and e_2 of such a thick lens may be regarded as two thin elements separated by an air space equal to t/μ , μ being the refractive index. This manner of regarding the case corresponds to the Gaussian or first-order system.

Practical experience as well as further theoretical investigation has fully confirmed my confidence in the soundness of this method of treating complex lens

problems as compared with any method involving formulae which purport to apply to thick lenses as a whole. Formulae of the latter character become undesirably complex and unwieldy, owing largely to the fact that lens-thicknesses necessarily involve very serious changes in Coddington's vergency parameters α and β relating to the second surface or element.

For, if these parameters truly represent the vergencies of the rays and principal rays respectively traversing the first surface yet, if the lens be thick, they seriously fail to express in a convenient form the vergencies of the same rays traversing the second surface.

Such formulae, purporting to make use with sufficient accuracy of the vergency parameters α and β as applied to any thick lens as a whole, are undesirably complex, and this objection will be found to be still stronger when it comes to working out formulae of the third and higher orders, which are often of too much importance to be negligible, as for instance in the case of wide-angle and rapid photographic lenses used for architectural views and for aerial survey or process-copying work, in which cases it is vitally important that the photographs shall be as free as possible from any curvature or distortion affecting the images of straight lines.

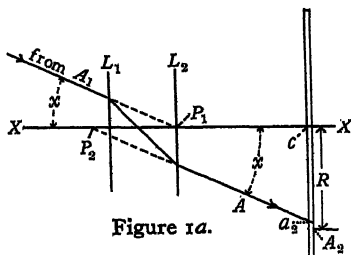


Figure 1a.

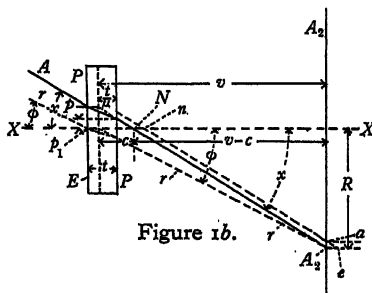


Figure 1b.

I will now supplement and extend the investigation of the effect of a parallel glass plate upon the distortion of images projected through it, and the formulae expressing such distortions, which are given on pages 266 to 268 of my book *A System of Applied Optics*.

Figure 1b represents an element E projecting an image at a distance v behind it, on to the focal plane A_2 , the projection being through the parallel glass plate PP .

In this case my second formula No. 17 (page 80) gave for the linear axial aberration Nn or A_2e of the second order $\{(\mu^2 - 1)/2\mu^3\} a^2/v^2$, in which μ is the refractive index, and the a^2/v^2 is obviously identical with $(pp_1/c)^2$ of figure 1b, or the square of the tangent of the angle of obliquity χ .

On page 267 was given the second-order formula (23) for the linear vertical or radial displacement aA_2 of figure 1b, which is obviously equal to the above linear-aberration formula multiplied by $\tan \chi$; therefore the formula for A_2a is $(\mu^2 - 1/2\mu^3) \tan^3 \chi$.

Then, if N is the point at a virtual distance c from the plate where the principal ray under first-order conditions crosses the optic axis XX , then the proportional distortion is expressed as the radial displacement A_2a in the image field A_2A_2

divided by R , the radial distance from the axis, and in this case $R = (v - c) \tan \chi$, so that the second proportional distortion is

$$t \left(\frac{\mu^2 - 1}{2\mu^3} \right) \tan^3 \chi / (v - c) \tan \chi, \text{ which } = t \left(\frac{\mu^2 - 1}{2\mu^3 (v - c)} \right) \tan^2 \chi \dots\dots(1).$$

This is the formula for the second-order proportional distortion (24) given on page 268 of my book. It is obvious that if R , the radius of the field to point A_2 , is to be expressed in terms of the focal length v and of the tangent ϕ which has reference to the centre of element E , then the above formula (1) becomes

$$t \left(\frac{\mu^2 - 1}{2\mu^3 (v)} \right) \tan^2 \phi \dots\dots(1a),$$

which gives the same result as (1). It should be noted that all such lifting or side-stepping of rays caused by their passage through the three parallel glass plates of figures 1 and 2 implies a distortion that is negative or towards the optic axis, but

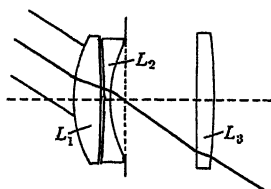


Figure 1.

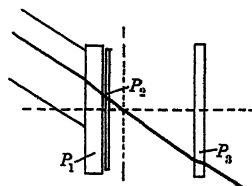


Figure 2.

that their effects upon the distortion of the final image formed by the lens system is a matter to be treated in two alternative ways, with similar results: (a) on the simple principle of each lens element in its turn copying through all the errors in the images presented to it*, and the other (b) to be explained in my next paper.

Also it is clear that any glass-thickness formulae which allow for (i) the obvious decrease of thickness, as measured by the versines of the lens curves of positive thick lenses, which takes place as the rays, when traversing the lens, recede from the lens axis, and (ii) the corresponding increase of the thickness in the case of negative lenses, will take the form of formulae of the third and higher orders only. Such formulae of the third order will be given later.

The first-order method of stating the effect of a parallel plate upon all rays traversing it obliquely is based on the assumption that

$$\tan (\text{angle of refraction}) = \tan (\text{angle of incidence}) / \mu \dots\dots(1b),$$

and therefore the effect upon any ray after emergence is simply to move it forward or side-step it parallel to itself through a distance (which is constant for all rays and is measured perpendicular to the plate) equal to $t (\mu - 1) / \mu$. Under such a first-order premise only, any aberration dependent upon the true relation between the angles of incidence in air and the angles of refraction within the glass is entirely ignored.

* Described in *A System of Applied Optics* (page 262 et seq.).

But the second- and higher-order formulae are based upon the correct law

$$\sin(\text{angle of refraction}) = \sin(\text{angle of incidence})/\mu \quad \dots\dots(1c),$$

which necessarily implies aberrations from the first-order formulae dependent upon the angles of incidence of the rays upon any parallel plate of thickness t .

The formula for the linear displacement or side-stepping parallel to the optic axis Nn or A_2e in figure 1*b* of a ray (analogous to linear spherical aberration) is, when expressed by the first four orders,

$$t \left\{ \frac{\mu^2 - 1}{2\mu^3} \tan^2 \chi - \frac{3(\mu^2 - 1)^2}{8\mu^5} \tan^4 \chi + \frac{5(\mu^2 - 1)^3}{16\mu^7} \tan^6 \chi - \frac{35(\mu^2 - 1)^4}{128\mu^9} \tan^8 \chi \right\} \dots\dots(2).$$

Then the linear side-stepping vertical to the optic axis is obviously the above formula multiplied by $\tan \chi$.

The first two terms of what is an infinite series of converging overstatements alternating with understatements of the correct aberration serve well enough for most practical purposes, while the third and fourth terms may occasionally be useful when greater exactitude is required, as in cases wherein different orders have to be separately stated in order that they may be added to the corresponding orders of the other sorts of distortion aberrations due to the same rays traversing the lens elements of the combination.

It is unfortunate however that this formula (2) involves a series of alternating + and - terms whose summed-up results diminish so gradually in accuracy that if errors of more than 5 per cent in the total are to be avoided, while the orders are kept distinct, then all the first four terms must be retained if the angle of obliquity χ exceeds 30° .

For instance, the first (or second-order term) generally exceeds the correct trigonometrical value of the linear aberration Nn or A_2e of figure 1*b* by about 44 per cent if $\chi = 45^\circ$, by 13 per cent if $\chi = 30^\circ$ and by 4 per cent if $\chi = 15^\circ$, when μ is about 1.60.

It is clear that this side-stepping, as it were, of a ray after passage through a parallel glass plate, without the occurrence of any angular deviation except within the plate, distinguishes it from all other aberrations produced by the refraction of rays through lens surfaces or elements, for in the latter cases an alteration of direction or angular deviation is always imparted unless, of course, the ray traverses the centre of a thin lens or element, or passes perpendicularly through a glass surface or glass plate.

Therefore, if the effect produced in the final focal plane of an optical system has to be computed, the effects of the glass-thicknesses involved in the various lenses must be worked out separately by specially appropriate formulae, and for the purpose of working out such formulae and illustrating their application I thought I could scarcely do better than to take the case of the original (Series V) Cooke lens, whose section is given in figure 1. Figure 2 is schematic and simply represents the six element planes, each of the three pairs thereof being separated by intervals equal

to t/μ which expresses the equivalent air spaces, in accordance with the Gaussian or first-order point of view. The equivalent focal length is 10 inches.

Figure 3 represents, on a larger scale and schematically, the effects which follow in the case of the first or front lens L_1 of figure 1. Here the hypothetical parallel glass plate of the lens (whose thickness $t = 0.299$ in.) is represented, while the thick black line E_1 on the first surface represents the first positive refracting element plane as a first-order refracting plane which has an equivalent focal length of 2.383 in. The thin black line represents the second element or refracting plane, which is also the second surface of the parallel glass plate.

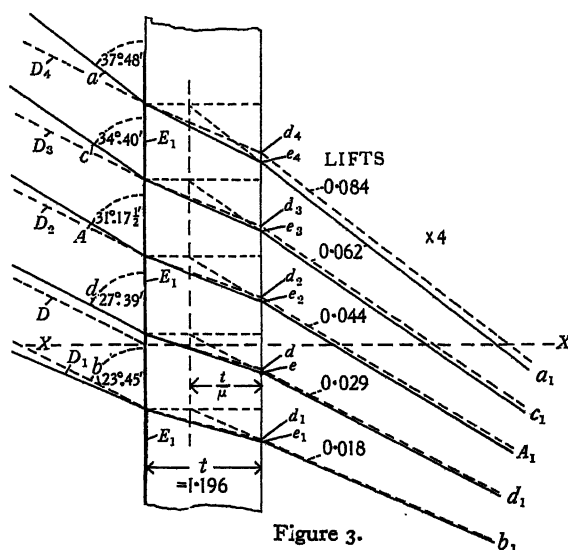


Figure 3.

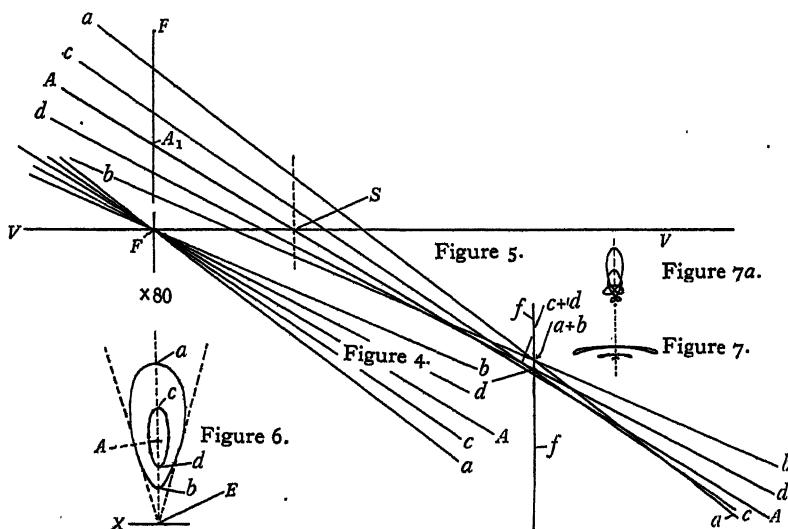
The dashed line XX is the optic axis, while the dotted entering ray D is that oblique ray from a distant object which passes through the centre of the first element, of course without being deviated, while D_1 , D_2 , D_3 , and D_4 are also parallel to D and are the other four of the pencil of parallel rays coming from the same point in the distant object on the left. D_2 is the central ray of the oblique pencil of five rays and is regarded as the principal ray, as it passes the centre of the stop.

But after being refracted by the first element E (in accordance with first-order or Gaussian premises) these five parallel rays constituting an oblique pencil are all converged towards a point F in the principal focal plane of E_1 , where the ray D continued strikes the said focal plane; and the converging lines A , d , b , c and a are continuations backwards of the rays after their refraction through the first-element plane E_1 . Therefore these converging lines obviously represent the rays which impinge upon and then are all refracted through the parallel glass plate of thickness t .

The angle of obliquity with which the unrefracted ray D enters the parallel plate is here 27° , and from this the angles of obliquity of each of the other five rays after their respective refractions by E_1 are calculated. Of course these angles of obliquity refer to the perpendiculars and are restored after emergence from the glass plate.

Within the glass plate the full black lines indicate the courses of the rays according to the first-order or Gaussian assumption that $\tan(\text{angle of refraction}) = \tan(\text{angle of incidence})/\mu$, whereas the dotted lines or rays across t and their refracted continuations to the right after emergence indicate the rays as actually refracted according to the correct law that $\sin(\text{angle of refraction}) = \sin(\text{angle of incidence})/\mu$.

In this case the vertical separations or lifts shown between the same rays refracted under the first-order or Gaussian premise and under the exact law are given in inches for each ray to three decimal places, but multiplied by 4 to suit the $\times 4$ scale of the original. Also, since there is no reason why the different orders of



parallel-plate aberrations should be separately stated in this case, I thought it best to calculate the amounts of the vertical lifts l, l_1, l_2 , etc. by the exact trigonometrical method, the formula being

$$l = \frac{t \tan(\text{angle of incidence})}{\mu} - t \left\{ \tan \text{ of angle whose sine} = \frac{\text{sine of angle of incidence}}{\mu} \right\}.$$

The vertical lift or side-stepping of these several rays, due to their passage through the first element under first-order conditions and then through the plate, brings about an effect in the focal plane of E which is illustrated in figures 4 and 5, on a 40-times' scale of magnification.

Instead of all the rays being converged by E_1 to a focus at the proper position F , figure 4, they are all lifted up parallel to themselves but by varying amounts, so that they severally cut the focal plane FF of E_1 at the points shown in figure 5 and then pass on convergently beyond the focal plane to the nearest approach to a focus, in the form of an inward pseudo-comatic flare from the axial ray AA_1 to $a + b$, figure 5.

The lift from F to A_1 of the principal ray A , figure 5, is the linear distortion of

position in the image field; the horizontal distance F to ff is the linear over-correction or throwing back of the field brought about by the glass plate. The rays refracted in the primary plane (the plane of the paper) form the inward pseudo-comatic flare at A , $c + d$ and $a + b$, figure 5, whose section in a plane perpendicular to the paper is indicated roughly in figure 7. In the secondary plane, perpendicular to the paper and the optic axis, the extreme upper and lower rays which enter the element E_1 above and below the principal ray D_2 intercrossover or come to focus somewhere about S , figure 5, where a pseudo-comatic flare, figure 7a, with its long axis lying in the plane of the diagram and pointing to the optic axis XX , is formed. Then the distance S to f between the two comatic flares is the linear astigmatism,

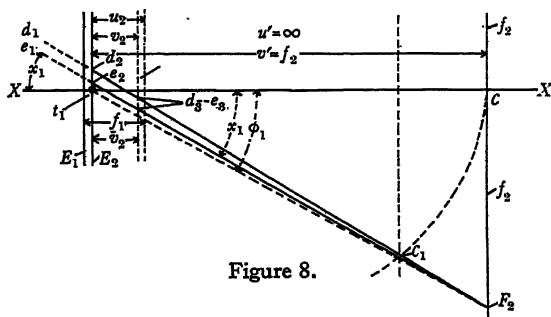


Figure 8.

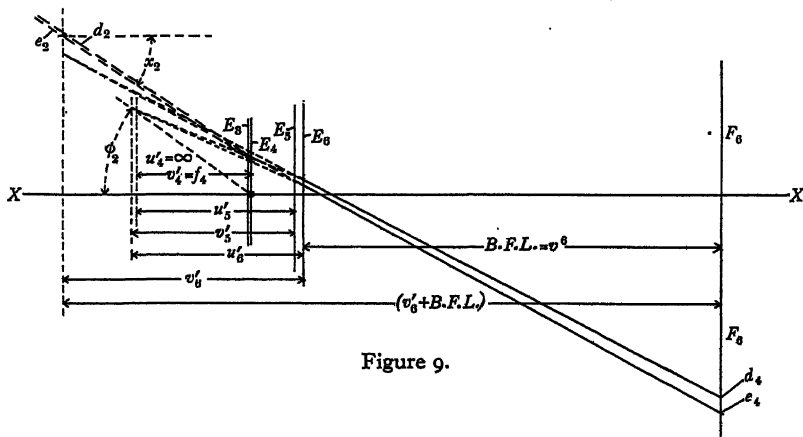


Figure 9.

which is in this case about equal to the linear over-correction of field F to $f \times 0.625$. At smaller angles of obliquity this ratio approaches 0.66. Figure 6 represents the oval out-of-focus patch of light formed in the focal plane FF' , in which A , a , b , c and d are the striking points of the principal and four other rays represented in figures 3 and 5.

It is clear that the varying parallel displacements, towards the optic axis, of the rays contained in the oblique pencil are the cause of, firstly, the displacement of the central or principal ray from its proper alignment through F , which is the linear distortion, and secondly the production of the two stigmatic and comatic formations at A and S , figure 5, separated by the horizontal stigmatic distance S to ff ;

thirdly, the two horizontal distances F to f and F to S are the linear values of the two field corrections (or departures from normal field curvatures) F to ff in the primary plane and F to S in the secondary plane.

All these aberrations thus have their cause in the passage of a convergent oblique pencil through any parallel glass plate occurring in a lens system. But the aberration of the first importance, so produced, is that of the linear distortion FA_1 , figure 5, while the next in importance are the accompanying comatic formations, figures 7 and 7a.

With regard to the distortion, I have previously given the formula (2) expressing in four orders (2nd to 5th) the linear aberration measured parallel to the optic axis and caused by the parallel plate. Also, if formula (2) is multiplied by $\tan \chi$,

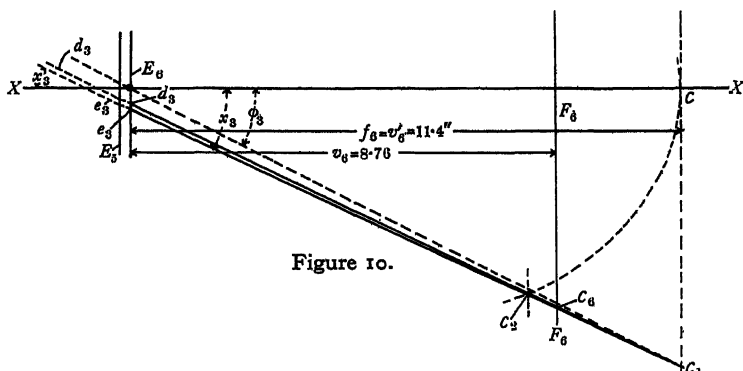


Figure 10.

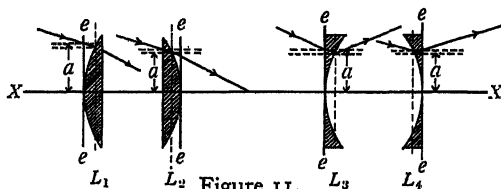


Figure 11.

we then get the radial linear distortion in the image field, and since we want the radius of the image field (or $v \tan \phi$) to be the unit, and to express the linear distortion as a percentage of that unit, then we arrive at

$$\frac{\text{Formula (2)} \tan \chi}{v \tan \phi \text{ or } (v - c) \tan \chi},$$

in which $v \tan \phi$ and $(v - c) \tan \chi$ are equal alternative expressions in the fractional distortion of image. Or, more fully, we get

Fractional Distortion

$$= \frac{t}{v - c} \left\{ \frac{\mu^2 - 1}{2\mu^3} \tan^2 \chi - \frac{3(\mu^2 - 1)^2}{8\mu^5} \tan^4 \chi + \frac{5(\mu^2 - 1)^3}{16\mu^7} \tan^6 \chi - \frac{35(\mu^2 - 1)^4}{128\mu^9} \tan^8 \chi \right\} \dots (3),$$

as in figure 1b in which χ is the angle of incidence on the plate of the principal ray dealt with, and not the angle of obliquity ϕ subtended by R at the centre of E , the

first of the two elements enclosing the parallel plate. It is the finely dotted ray rr in figure 1*b* that is inclined to the axis XX at the angle ϕ .

Of course it is easier to calculate the exact linear aberration of a glass plate trigonometrically by formula (1) than by the above formula (3) with its two, three or four orders, but, when one is working out the aberrations of lens systems to the degree of accuracy required for a very high standard of performance, it is of essential importance to be able to sum up all the second-order formulae which express the fractional distortions of the system and keep them separate from the third-order distortion formulae and the latter from the fourth-order, and so on.

For instance, one cannot equate to 0 or balance off second- and third-order distortions (functions of $\tan^2\chi$ and $\tan^4\chi$) for a point in the final focal plane situated, say, 33° from the axis, without necessarily implying a zone of hybrid distortion which exerts its maximum effect at an angle θ such that $\tan \theta = \tan 33^\circ \div \sqrt{2}$.

It is well known that most so-called rectilinear photographic lenses, and especially wide-angle ones, show no linear distortion at, for instance, a point in the field 27° from the centre, but show a maximum of negative distortion at an angle whose tangent is $\tan 27^\circ \div \sqrt{2}$ and a rapidly increasing positive distortion at angles greater than 27° .

So that, if no zone of hybrid distortion is to be allowed in the final image field of any particular lens combination, it is necessary to arrange that the sum of the third-order distortion formulae of the combination shall equate to 0 simultaneously with the sum of the second-order distortion formulae of the same combination also equating to 0, as nearly as possible.

DISCUSSION

Mr T. SMITH. This paper should be regarded as a supplement to the author's book *A System of Applied Optics*. Perhaps the most illuminating parts of the whole discussion are figures 5, 6, 7, and 7*a*: these convey most valuable information to the designer of instruments. As the author has indicated on p. 286, the slowness with which the first few terms of the series give a sufficiently exact result is sometimes a cause of difficulty, but I think it would be helpful if the figures were supplemented by others showing the outstanding errors in terms of the axial thickness of the plate. This would give a common measure for the different cases considered.

There are often strong inducements to refrain from, or at least to delay, publication of work of this kind, but in the long run there can be little doubt that prompt publication makes for the most rapid advancement of the art of designing in which the author has achieved such notable success. We are indebted to him for the public-spirited way in which he gave us the benefit of his long and arduous investigations in his book, and for the way in which he has followed up that work in his papers. I can only hope that the gratitude we express now to Mr Taylor will lead other workers in this field to realize how very warmly contributions from them to our knowledge would be welcomed by us.

THE MEASUREMENT OF THE INDUCTANCE OF IRON-CORED CHOKES CARRYING DIRECT CURRENT

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Communicated by Prof. T. H. Laby, July 10, 1933. Read January 19, 1934.

ABSTRACT. A method for measuring, by means of a reflecting dynamometer ammeter, the inductance of an iron-cored coil is described. The coil is connected in series with a capacity and the ammeter, and then the junction of the inductance and capacity and the junction of the fixed and moving coils are connected to an a.-c. supply. It is shown that for a constant applied voltage the deflection of the dynamometer ammeter is proportional to the square root of the reciprocal of the inductance. This is also true when a direct current is superimposed on the alternating current flowing through the inductance. Advantages of the method are the simplicity of the measuring instruments and of the observations taken, the small value of the alternating current used (which corresponds to the alternating current in certain applications of chokes in wireless sets), and the independence of the method within wide limits of the frequency and wave-form of the supply used.

§ 1. INTRODUCTION

THE majority of existing methods of measuring the inductance of choke coils carrying direct current involve the comparison by means of a valve or thermocouple voltmeter of the alternating potentials across the choke coil and a resistance in series with it, in a circuit carrying both direct and alternating currents. A good outline of this method is available in a paper by H. B. Dent*, and by a method of this type measurements of the inductance of iron-cored choke coils carrying direct current have been made by L. M. Turner† and by Wright and Bowditch‡.

A very ingenious method of making these measurements is given by H. M. Turner‡. It uses simple laboratory apparatus, but requires a standard variable condenser and, in common with the above method, an accurate knowledge of the frequency. The present method, on the other hand, is practically independent of frequency.

* *Wireless World*, 26 August (1931).

† *Wireless Engineer*, 4, 594 (1927).

‡ *Proc. Inst. Radio Eng.* 16, 1559 (1928).

§ 2. PRINCIPLES OF METHOD

The actual and equivalent circuit diagrams are shown in figures 1 and 2.

For the branch of the circuit containing the choke coil let r_L ohms be the resistance, L henries the inductance and I_L amperes the alternating current through the choke; and for the branch of the circuit containing the condenser let r_C ohms be the resistance, C farads the capacity, and I_C amperes the current through it, while f cycles per second is the supply frequency, and $p = 2\pi f$. Then if r_L is negligible compared with Lp , and r_C is negligible compared with $1/Cp$, the current through the choke will lag behind the applied voltage V by 90° , and be of magnitude V/Lp , while the current through the condenser will lead the applied voltage by 90° and be of magnitude CpV .

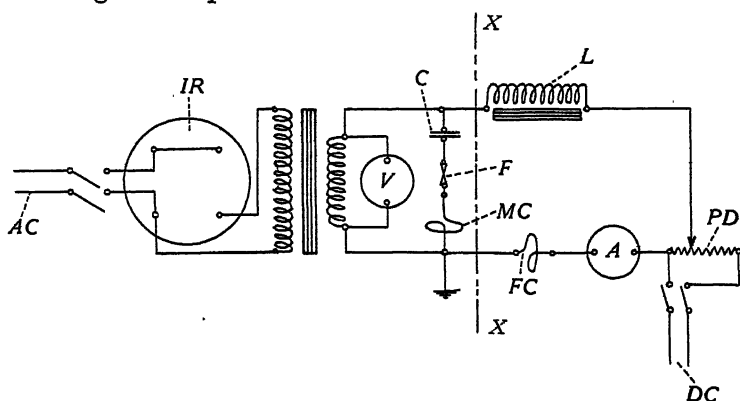


Figure 1. *AC*, a.-c. mains; *IR*, induction regulator; *V*, a.-c. voltmeter; *C*, condenser of C farads; *L*, choke of L henries; *F*, fuse; *MC*, moving coil and *FC*, fixed coil of dynamometer ammeter; *A*, d.-c. ammeter; *PD*, potential-divider; *DC*, battery.

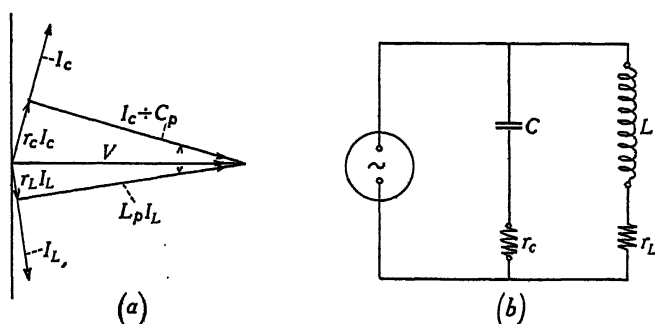


Figure 2. (a) Vector diagram. (b) Equivalent circuit.

Then the deflection d of the dynamometer ammeter, being independent of direct current flowing through the fixed coils only, will be given by

$$d = k \sqrt{\left(pCV \times \frac{V}{Lp} \right)} = kV\sqrt{C/L} \quad \text{.....(1),}$$

where k is a calibration constant.

Hence

$$L = k^2 V^2 C / d^2 \quad \dots\dots(2).$$

This formula is independent of the frequency.

Thus for fixed voltage and capacity, the inductance is inversely proportional to the square of the dynamometer ammeter reading.

§ 3. MAGNITUDE OF ERRORS

Accuracy of formulae. Case (i) In the normal case of measurement with a suitably designed instrument r_L/Lp and Cpr_0 are both small, and on consideration of the vector diagram of figure 2, the actual ammeter reading d is seen to be given by

$$d = k\sqrt{I_0 I_L \cos \phi} = k \left[\frac{V^2}{(r_0^2 + 1/C^2 p^2)(r_L^2 + L^2 p^2)} (Lp/Cp - r_0 r_L) \right]^{\frac{1}{2}} \quad \dots\dots(1),$$

therefore to the first order,

$$d^2 = (k^2 V^2 C / L) (1 - r_0^2 p^2 C^2 - r_L^2 / L^2 p^2 - r_0 r_L C / L).$$

Thus L is seen to be less than $k^2 V^2 C / d^2$ by the fraction

$$(r_0^2 p^2 C^2 + r_L^2 / L^2 p^2 + r_0 r_L C / L)$$

of its value.

In practice Cpr_0 and r_L/Lp are both less than 0.05, so that the correction becomes less than 3 parts in 400, which is negligible.

Case (ii) If when an existing dynamometer instrument is being used as a make-shift, Cpr_0 and r_L/Lp attain values so large that $(Cpr_0)^4$ or $(r_L/Lp)^4$ are not negligible, so that the corrections discussed in case (i) are unsuitable, it is then necessary to use the equation

$$L = \frac{1}{2} L_1 (1 + \sqrt{x}),$$

where

$$L_1 = \frac{k^2 V^2 C}{d^2 (1 + C^2 p^2 r_0^2)}$$

and

$$x = 1 - 4 [(r_L/L_1 p)^2 + r_0 r_L C / L_1],$$

a formula readily derived from equation (1).

Dynamometer inductances. In the theoretical treatment given above the inductances of the moving and fixed coils and their mutual inductance M have been neglected, and normally this is quite justifiable in view of their low values as compared with the inductance to be measured; but when in the measurement of inductances with low applied a.-c. voltages I_0 is increased to give a satisfactory deflection, the term MpI_0 may cause an appreciable voltage-error. For example in the apparatus described in § 5 for a 50-henry choke coil $MpI_0 = 10$ mV. when $V = 0.5$ V., and under these conditions the lowest workable value of V is about 1 V. For low a.-c. voltages it was found convenient to place between the portions of the circuit to the left and right of XX , figure 1, a 100:1 step-down transformer which enabled 200 volts to be applied to the condenser with 2 volts across the inductance. This permits a smaller condenser to be used and the formula $L = k^2 V^2 C / 100 d^2$ holds, the elaborate corrections of case (ii) being now un-

necessary; and further the extra transformer is used under light-load conditions, so that corrections for its voltage-ratio and phase-angle are negligible.

The d.-c. potentiometer. Normally the potentiometer-resistance is variable and is included in r_L , but in case (i) the corrections containing r_L as a factor are negligible or only first-order terms, and so the changes in r_L have no effect. In case (ii) it is necessary to keep constant the potentiometer resistance included in r_L , and this is achieved within close limits by keeping constant the potentiometer resistance in the inductance circuit, keeping it low in value, and varying the d.-c. potential-drop across it by means of battery taps and resistance in the battery circuit. When low-impedance chokes are being measured the potentiometer resistance may be made very small by using an accumulator battery with terminal taps and a low resistance potentiometer across the end cell, all in series with the inductance to be measured.

It will now be shown that if a dynamometer voltmeter is used, any harmonics present in the secondary voltage will produce substantially no effect on the voltmeter and ammeter readings.

Voltmeter reading. If the instantaneous voltage across the secondary of the transformer is \bar{V} , where

$$\bar{V} = V_0 + \sqrt{2} [V_1 \sin pt + V_2 \sin (2pt + \phi_2) + \dots + V_r \sin (rpt + \phi_r)]$$

and V_0 is the d.-c. voltage-drop in the transformer winding;

V_r the root-mean-square value of r th voltage harmonic; and

ϕ_r the phase difference between \bar{V}_r and \bar{V}_1 ,

then the reading V of the dynamometer voltmeter will be given by

$$V = (V_0^2 + V_1^2 + \dots + V_r^2 + \dots)^{\frac{1}{2}}$$

and the effect of V_0 may generally be neglected; for if V_m is the maximum d.-c. voltage applied to the circuit by the potentiometer and r, R the resistances of the transformer secondary and the circuit connected across the potentiometer, then $V_0 = (r/R) V_m$, which in practice can readily be made less than 0.05 V., by the use of a transformer with a low-resistance secondary. Since this value of V_0 affects the value of V only to the extent of $\frac{1}{2} (0.05)^2 V$, or $1/800 V_1$, it is negligible.

Ammeter reading. With the applied voltage \bar{V} the current through the inductance will, to the first order, be

$$\frac{V_m}{R} + \frac{V_1}{Lp} \sin \left(pt - \frac{\pi}{2} \right) + \frac{V_2}{2Lp} \sin \left(2pt + \phi_2 - \frac{\pi}{2} \right) + \dots + \frac{V_r}{rLp} \sin \left(rpt + \phi_r - \frac{\pi}{2} \right)$$

while the current through the condenser will be

$$CpV_1 \sin \left(pt + \frac{\pi}{2} \right) + 2CpV_2 \sin \left(2pt + \phi_2 + \frac{\pi}{2} \right) + \dots + rCpV_r \sin \left(rpt + \phi_r + \frac{\pi}{2} \right)$$

and these currents will produce a reading of the dynamometer ammeter equal to

$$k \left\{ \frac{C}{L} (V_1^2 + V_2^2 + \dots + V_r^2 + \dots) \right\}^{\frac{1}{2}}.$$

Thus if a dynamometer voltmeter is used and the secondary voltage V is kept constant, the effect of voltage harmonics will cancel out.

§ 4. EXPERIMENTAL DETAILS

Apparatus. The following instruments are required: (i) A permanent-magnet moving-coil ammeter, to measure the direct current. (ii) A dynamometer ammeter whose fixed coil is capable of carrying the maximum direct current through the choke, and whose moving coil should preferably have a current capacity greater than that of full-scale reading. (iii) A transformer to give the required voltage V , with an isolated secondary to prevent the d.-c. battery from being at a high potential above earth. (iv) An a.-c. voltmeter, preferably of the dynamometer type, with a sensitive movement. (v) An induction regulator in the transformer primary to keep the secondary voltage V constant. Although this is not absolutely necessary it greatly simplifies the method, as regards both the taking of readings and the working out of the results. An induction regulator gives smoother adjustment than primary resistances. (vi) A potential-divider to introduce the direct current. (vii) A condenser of good insulation resistance and known capacity C farads, to be selected to suit the measurement required. This apparatus is connected as shown in figure 1.

Design of dynamometer instrument. In all cases the fixed coils must have a current capacity at least equal to D , the largest direct current to pass through the choke coils to be tested. Then for maximum range of inductance-measurement it is advisable to have the current capacity of the moving system at least $0.1D$ and to select the suspension so that the full-scale deflection is approximately $0.01D$. In conjunction with this, it is advisable to keep the resistances of the fixed and moving coil systems as low as possible.

For wireless applications it was found convenient to have D equal to 500 mA., with a phosphor-bronze suspension to carry the moving-coil current.

Setting up the apparatus. To do this to best advantage, it is necessary to know the range of use of the dynamometer ammeter, which is decided as follows. If the satisfactory range of the ammeter scale is between i_0 and i_1 , then I_L and I_G are limited by the relation $i_1^2 > I_G I_L > i_0^2$ and the current-carrying capacity of the fixed and moving coils. Thus if V volts a.-c. be the voltage at which the inductance is required, and l a rough estimate (within several hundred per cent) of the inductance, a guide to the selection of a suitable value of C is given by

$$C = \frac{l}{V^2} \left(\frac{i_0 + i_1}{2} \right)^2.$$

Procedure. A value of C having been selected and the resistance of the choke measured, the apparatus is connected as shown in figure 1. The direct current is set to the required value as indicated by the d.-c. ammeter, an a.-c. voltage is switched on and adjusted to the value V by means of the induction regulator, and the reading d of the dynamometer ammeter is taken. From these readings a value of L is calculated according to the formula $L = k^2 V^2 C / d^2$, and the values of $r_L / L \rho$ and $C \rho r_G$ are determined, enabling us to select the method of working out the results.

§ 5. EXPERIMENTAL RESULTS

A number of graphs of inductance were plotted against direct-current-strengths for different applied a.-c. voltages, and were found to agree with those of L. M. Turner. The results were all taken with a direct-reading dynamometer milliammeter giving a full-scale deflection with 6 mA. It had fixed and moving coils of 89 and 85 ohms respectively, the current capacity of the fixed coils being approximately 500 mA., while that of the moving system was limited by the suspension to about 50 mA. The resistance of the instrument is rather inconveniently high for the measurement of low-impedance choke coils; but this defect makes it suitable for illustrating the procedure when large corrections occur, an event which would but rarely arise with a specially designed instrument.

For the following observations a.-c. mains with p equal to 314.2 were used as the source of power, and r_L was equal to 85 ohms throughout.

Table 1. These results were taken on a commercial choke coil rated at 230 henries at 5 mA. d.c. Its resistance was 3800 Ω ,

V was 85 V., C was $0.292 \mu\text{F.}$, and r_L was 4000 Ω .

Hence $Cpr_0 = 0.0078$ and $r_L/Lp = 0.056$, so that both are negligible.

$$V^2C = 85^2 \times 0.292 \times 10^{-6} = 2110 \times 10^{-6}.$$

Table 1

Direct current (mA.)	Dynamometer reading I (mA.)	L , or $2110/I^2$
0	2.215	431
4	2.665	296
8	2.970	240

Table 2 relates to a stalloy choke coil with no air gap, rated at 20 H. with no direct current. Its resistance was 84 Ω ., r_L was 180 Ω ., V was 2.01 V., and C was $19.4 \mu\text{F.}$, so that $V^2C = 78.45 \times 10^{-6}$, and $Cpr_0 = 0.518$.

Thus $(Cpr_0)^4 = 0.072$, and the results must therefore be calculated according to case (ii) of § 3.

$$V^2/\{1 + (Cpr_0)^2\} = 61.8 \times 10^{-6}; \quad 4r_0r_LC = 1.19; \quad \text{and} \quad 4(r_L/p)^2 = 1.31.$$

Table 2

Direct current (mA.)	Dynamometer reading (mA.)	L_1 , or $61.8/I^2$	$\frac{1.19}{L_1}$	$\frac{1.31}{L_1^2}$	$\frac{1.19}{L_1} + \frac{1.31}{L_1^2}$	x	$1 + \sqrt{x}$	L , or $\frac{1}{2}L_1(1 + \sqrt{x})$
0	1.575	24.9	0.048	0.002	0.050	0.950	1.975	24.6
10	2.230	12.4	0.096	0.008	0.104	0.896	1.945	12.1
50	3.600	4.76	0.250	0.058	0.308	0.692	1.832	4.36
100	4.615	2.90	0.411	0.156	0.567	0.433	1.657	2.40

§ 6. ADVANTAGES OF THE METHOD

The dynamometer ammeter is extremely simple and is readily made in any laboratory, and the calibration can be simply carried out with reversed direct current; the method is independent, within wide limits, of wave-form and frequency; the range of measurements covered by any one instrument is large; measurements may be made with very small a.-c. currents passing through the choke coil—down to 0.04 mA. for the dynamometer used in the experimental work; and only one reading has to be recorded for each observation, the dynamometer reading being taken when the voltage is brought to the correct value, while small supply-frequency variations are neglected.

§ 7. ACKNOWLEDGMENTS

This work was carried out in the Electrical Engineering Laboratory of the University of Melbourne under the terms of the Robert Bage Memorial Scholarship Award for 1933.

I wish to thank Prof. T. H. Laby, M.A., D.Sc., F.R.S., for his advice and assistance in the arrangement of the paper.

DISCUSSION

Dr D. OWEN. The author has applied the electro-dynamometer to the measurement of the inductance of iron-cored chokes carrying direct current, a condition which is usual in many valve circuits. The use of the condenser in series with one of the coils of the instrument surmounts the difficulty arising from the presence of the direct current.

It is, however, misleading to term the instrument employed a dynamometer ammeter, since the two coils are not in series. In the section on the design of the dynamometer the question of the most suitable windings for the two coils might with advantage have been treated. It is fairly clear that for the present application the corrections required, when the formula is used in its simplest form, will be diminished by making the resistance of the coil in series with the condenser as low as possible, while the second (fixed) coil may have many more turns and a much larger resistance, in order to retain the desired sensibility.

In regard to the experimental data quoted it should be made clear that it is the a.-c. resistance that is required in applying the appropriate corrections to the simple formula (1). The importance of these corrections is consequently underestimated in the examples used in the paper.

It may be noted that the error which in certain cases may arise from the induced voltage injected by one coil into the other can be eliminated by taking a second reading with the connections to one of the coils reversed. But it is possible to avoid this source of error altogether by modifying the method so that it becomes a null one. It is hoped to investigate this possibility by experiment.

AUTHOR'S reply. Dr Owen's criticism of the use of the term "dynamometer ammeter" to specify the instrument is quite justified and the word could be replaced

by "electrodynamometer", for in some applications of the method a dynamometer wattmeter was used and a ratio of fixed to moving coil currents of 10,000 to 1 arose. The design of the instrument is in no way critical, and any dynamometer with a sensitive movement, a low-resistance moving-coil system and large number of turns on the fixed-coil system will cover a large range of measurements. The size of winding-wire is suitably determined by the current capacities suggested, and the diameter of the coils is selected according to whether spring or single-wire suspension is adopted. The moving-coil system is made up of as many turns and as low a resistance as possible, 50 ohms being a suitable value; then with I_0 maximum flowing through the moving coils the a.-c. ampere-turns of the fixed coils must be sufficient to give a suitable deflection with a current equal to V/Lp , minimum, flowing through them.

These ampere-turns are most simply found by mounting the moving-coil system and finding the current required through a few heavy turns mounted on the fixed-coil formers, to give the desired deflection. It can then be considered whether it would be advisable to use a more sensitive suspension with fewer fixed-coil turns, and care should be taken to keep the mutual inductance between the moving and fixed coils as low as is compatible with a reasonably robust suspension.

The error in taking r_L as the d.-c. instead of the a.-c. resistance of the choke coil will generally be of no consequence, for on low frequencies the approximation is satisfactory and r_L/Lp decreases in importance with frequency; moreover r_L/Lp is in general quite a small correction term. However, when a high a.-c. voltage is applied across a low-impedance choke coil the possibility of iron losses increasing the equivalent r_L should be considered.

The suggested method of eliminating the effect of voltage induced in the moving coil by the fixed, in common with a number of compensation methods tried out, suffers from the disadvantage that on reversal of the connection to one of the instrument coils, the deflection is reversed. This necessitates a centre zero, which in reflecting instruments gives trouble owing to zero-creep.

I have given considerable thought to Dr Owen's suggestion that the method could be made a null one, and only two ways occur to me in which this could be done. (1) Place across the inductance a variable condenser and a variable resistance in series, and tune so that the parallel impedance is resistive. This method would be far too insensitive, for even though the reactive component of the impedance increases rapidly on either side of resonance, the impedance remains very large owing to the high L/C ratio usually met with in its range of use. (2) Use double-wound fixed coils, one half of the winding being in series with inductance and d.-c. potentiometer as in the circuit diagram, the other half in series with a variable condenser and resistance, and the two circuits being in parallel. This arrangement can be tuned to zero deflection, but the method will be no longer independent of wave-form and frequency, it will not be so convenient to use, and the apparatus required will be more elaborate. This plan should, however, be valuable for tuning low-frequency circuits under working conditions, for the iron in the choke coil can be brought to the same saturation as that in the plate circuit of a valve.

REVIEWS OF BOOKS

Theory of Thermionic Vacuum Tubes, by E. L. CHAFFEE, Professor of Physics, Harvard University. Pp. 652 + xxiii, with 347 diagrams and 6 plates. (McGraw-Hill, 1933.) Price \$6.00.

Great progress in the design and uses of the many forms of the thermionic tube is due to be recorded since the excellent treatise on this subject by Van der Bijl, which appeared in 1920 under the auspices of the same publishers. The author announces in his preface that the present volume is written primarily as a text-book, though he hopes it may serve also as a reference book. In view of its formidable size this must seem somewhat disconcerting to the student of physics or of electrical engineering, to whom the subject can rank only as one of many to be mastered, as well as may be, in the course of a normal university training. This feeling, moreover, will be accentuated when he learns that owing to the mass of material involved only the theory of vacuum tubes at low power is here included, and that the remainder, including the theory of power amplifiers, oscillators, gas-content tubes, rectifiers, etc., is held over for treatment in a subsequent volume.

But whether as text-book or for reference, this book will be found to contain an eminently sound treatment of the characteristic properties and multiform applications of hard thermionic tubes, and will be appreciated by all interested in the design and precise functioning of these devices. The first five chapters give an introductory account of the physics of the valve, of the various types of electronic emission, and of emitting materials. After a brief chapter allotted to nomenclature follow three chapters containing a treatment, partly analytical and partly graphical, of the actions within the triode valve, with its equivalent circuits and its six coefficients and the modes, static and dynamic, of their measurement. A chapter is given to the effect of the presence of slight traces of gas on the characteristics.

In all fifteen chapters are devoted to the triode, first as detector and then as amplifier both at audio- and radio-frequencies. The various types of multi-stage amplification, with and without regenerative action, at small amplitudes and at large amplitudes, are in turn dealt with. The modes of energy-interchange between grid and plate circuits of a triode are analyzed, as well as the means of nullifying or "neutralizing" this effect. The same combination of analytic and graphic treatment is applied in a final chapter on tetrodes and pentodes.

The book is well written and produced, the illustrations are abundant and excellent, and copious references are given to the literature of the subject. Space models as well as the usual two-dimensional characteristics are discussed and represented in clear photographs. A few points of criticism may be mentioned. First, the absence of reference to the magnetron. Next the brevity of treatment of the photoelectric effect, the normal effect only being described in the text, whilst the illustrative curves are confined to the selective effect. Again, the classification of amplifiers into classes *A*, *B* and *C* seems likely to cause confusion, in view of the different terminology largely in use now. It must, in conclusion, be again pointed out that the ground covered in this volume is only part, probably only half, of that indicated in the title. It would surely have been better to have made this fact quite explicit, by publishing the present book as volume 1 of the complete work.

D. O.

Physics for Medical Students. A supplementary text-book, by J. S. ROGERS, B.A., M.Sc., F.Inst.P. Edited by T. H. LABY, F.R.S. Pp. 197 (including two appendices) and index. 71 figures (including 6 half-plates). (Melbourne University Press in association with Oxford University Press.) 11s. 6d.

The title of this book rightly indicates that it has not been written to meet the needs of medical students who are reading for the pre-registration examination in physics. We judge that the writer had in mind medical students with an aptitude for physics who might wish for guidance in certain physical subjects that bear on general physiology and medical practice. Such students will find in the book under review brief but lucidly written chapters on certain aspects of so-called bio-physics (e.g. those on hydrogen ion concentration, osmosis, and colloids, though, strange to say, there is no chapter on surface phenomena) and of human physiology (e.g. those on blood pressure, the energy relations of the human body, the resonance theory of hearing, and the human eye) and on other physical topics (e.g. ultra-violet light, high frequency currents, X-rays, radio-activity, and the theory of the microscope) that concern the medical man. The book begins with a sketch of the history of physics.

M. T.

The Calculus of Finite Differences, by L. M. MILNE-THOMSON. Pp. xxiii + 558. (London: Macmillan & Co.) 30s. net.

To those who have not kept in touch with recent work in the theory of finite differences this book will come as a revelation. It falls roughly into two parts, seven chapters on interpolation and numerical work, with an account of the Bernoulli polynomials and certain generalizations of them, and ten chapters on the mathematics of the finite-difference equation.

The first section is well done, as must be expected from the author of *Standard Tables of Square Roots* and *Jacobi's Elliptic Functions*, and part-author of *Standard Four-Figure Tables*. It is, of course, only one of at least three good presentations of the subject in English, but it differs from the usual treatise in giving much more attention, with every form of interpolation formula, to tables which proceed by unequal increments of the argument.

The second part opens with a section on the summation problem for the equation of first order and degree, in which Nörlund's method is adopted. This is followed by a fascinating chapter on the difference equation of the first order, which Boole would have revelled in could he have lived to read it. It contains among other results the general solution to the complete linear equation of the first order, and a discussion of the theory of the exact equation of any degree. This chapter and the next two, on equations of the first degree but any order, cover practically all the ground that was known to Boole, though it is now presented in a rigorous form, in striking contrast to the vague arguments with which he had to be satisfied.

Chapter 14 deals with Milne-Thomson's extension of the operational method, first published in 1932. From this point to the end the book is not easy reading, largely owing to the strain on the memory due to the continual symbolism. With such a conspectus before one, it is possible to realize the present position of the theory of the difference equation clearly. It is surprising how much of the material is met with in treatises on analysis or on infinite series, and interesting to notice that practically all the processes familiar in the case of ordinary differential equations, except the application of group theory, now have their counterparts in the calculus of differences. Partial difference equations receive little consideration and apparently our knowledge of them has hardly increased in the last forty years.

The book under review is certainly not an elementary introduction to its subject, and should not be read by those whose knowledge of differential equations is less than can be obtained from the study of such a book as that by Ince. For those who are seriously hoping to learn something of the subject, there are examples in copious supply at the ends of almost all the chapters. Since examples are an essential aid to the understanding, as well as to the mental retention, of any book on mathematics, it is difficult to see why they are not invariably provided; and since they are so often absent it is only right to signalize the fact when they are present.

J. H. A.

Physical Constants, by W. H. J. CHILDS, B.Sc., Ph.D. Pp. viii + 77 with 7 nomograms. (London: Methuen & Co., Ltd.) 2s. 6d. net.

This book of tables of physical constants is an admirable example of bovrilization; it gives more useful information to the square centimetre than any other book of its kind with which the reviewer is acquainted. The contents are well arranged and selected, and, as far as the reviewer has tested them, accurate and up to date. An interesting feature is the use made of nomograms. The book should have a wide circulation; it may be strongly recommended.

A. F.

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A RELAY MEMORY FOR A THYRATRON COUNTER

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ABSTRACT. The paper describes an automatic mechanism consisting of sixteen inter-connected relays and capable of carrying out a complicated cycle of operations in correct sequence in less than half a second. The apparatus is used in conjunction with a valve amplifier and an automatic thyratron counter for the analysis of α -particle groups by means of a magnetic focusing method. The relay mechanism arranges for alternate comparative counts of α particles to be made under two different sets of experimental conditions, *A* and *B*. At the end of a 9-sec. counting period under condition *A*, a relay memory *A* records and remembers the thyratron-counter readings; a change-over of experimental conditions from *A* to *B* takes place, and another relay memory *B* restores the thyratron counter to the state at which it stopped at the end of the previous 9-sec. *B* count, from which point it continues to count under experimental condition *B*. In the meantime, memory *A* continues to remember its reading for 10 sec. until the next change-over, when conditions are restored to state *A* again, the cycle being repeated throughout the course of the experiment.

§ 1. GENERAL DESCRIPTION

IN a paper* published elsewhere, Lewis and Bowden describe an experiment which was carried out to investigate the fine structure of the α -particle groups from thorium *C* and thorium *C'*. As in previous experiments,† the α -particle groups were analysed by means of an annular magnetic field, and individual particles were counted by means of a valve amplifier and a thyratron scale-of-two automatic counter; for certain reasons, however, an entirely different method of working was adopted. Previously, the analysis had been carried out by focusing the various groups in turn on to the ionization-chamber slit, and, by suitably adjusting the strength of the magnetic field, exploring the region under investigation; the velocities of the particles in the various groups were then determined from the

* *Proc. R.S. A* 145, 854 (1934).

† Rutherford, Wynn-Williams, Lewis and Bowden, *Proc. R.S. A* 139, 617 (1933), and Rutherford, Lewis and Bowden, *Proc. R.S. A* 142, 347 (1933).

measurements of the strengths of the magnetic fields. In the more recent experiment, however, a method was adopted of measuring directly, in electron-volts, the energy-difference between two particle groups. This was done by maintaining the magnetic field as constant as possible at a value which would normally focus particles whose energies were equal to the mean value for the two groups, and applying alternately an accelerating and a retarding potential of $+10,000$ V. and $-10,000$ V. to the source. In this way, particles belonging to the two groups were in turn brought to a focus on the ionization chamber-slit, and alternate counts were made of the numbers of particles in the two groups. As Lewis and Bowden point out in their paper, this method has the great advantage of enabling one to pass instantly from one group to another, and also of enabling the energy-difference between the two groups to be measured directly in terms of the electric field, without involving a measurement of the strength of the magnetic field, provided the magnetic field is kept sufficiently steady during this process. In order that this latter condition may be realized, it is necessary to take alternate readings for the positive and negative potentials (which will be referred to in this paper as *experimental conditions A and B*), as frequently as possible, so that errors due to any slight inconstancy of the magnetic field will be negligible.

It is, of course, possible to carry out the change-over from condition *A* to condition *B* by hand, to take a large number of alternations in this manner, and to add up the two series of observations. Such a process, however, proved to be extremely tedious. Moreover, to enable the useful counting-time to be large compared with that required for the change-over operations, which would occupy several seconds, alternate counts of about half a minute would be necessary, and this would necessitate the change-overs being less frequent than is desirable. For this reason it is highly desirable in an experiment of this kind to devise and employ some form of apparatus to carry out all the operations automatically, so that this may be done with greater precision and speed and without the fatigue which is occasioned during the repetition of cycles of operations every half minute over very long periods.

Some idea of the operations involved in taking only a single pair of such observations, i.e. two half-minute counts, may be gathered from the following programme of instructions covering one cycle of events occupying a little over a minute. (1) Start counter and count for 30 sec. under condition *A*. (2) Switch off counter. (3) Record counter readings. (4) Reset counter. (5) Reverse electric field. (6) Start counter and count for 30 sec. under condition *B*. (7) Switch off counter. (8) Record counter readings. (9) Reset counter. (10) Reverse electric field.

The object of the present paper is to describe a form of automatic apparatus which has been devised for the purpose referred to and has proved highly efficient. The apparatus consists of sixteen relays, of the pattern used in telephone exchanges, interconnected in groups in such a way that it is impossible for them to operate in any but the correct sequence, and that a given relay operation cannot commence until the preceding operation has been correctly and completely performed. As will be seen later, there are nine stages in a change-over from one condition to the

other, and all the operations involved in the complete change-over are carried out by the relays in well under half a second. By this means it is possible to alternate the counts every 10 sec., 9 sec. being allowed for the count and 1 sec. for the complete change-over, so that there is a margin of at least half a second. It is estimated by Lewis and Bowden that the error involved on account of drift of the magnetic field during such short counts is not more than one part in two million.

As is well known, automatic relay mechanisms are extensively employed in connexion with automatic telephone exchanges and in many other branches of electrical engineering. In the past, however, little use seems to have been made of apparatus of this kind in connexion with purely physical problems. It is hoped that the present paper will serve to illustrate how a fairly complicated sequence of events can be carried out by such apparatus. There are many other physical problems to which relay mechanisms could be applied with great advantage, and the devising of suitable circuits is not very difficult when once the underlying principles have been grasped.

In what follows, it is assumed that the reader is acquainted with the principle of operation of the thyatron scale-of-two counter, which has been previously described*. It may be recalled, however, that with such a counter the natural numbers are recorded on a scale of two. Multiples of 8 or 2^3 are recorded on the dial of a mechanical counting meter, while numbers between 0 and 7, which are given by the addition of combinations of 2^0 , 2^1 and 2^2 , or 1, 2 and 4, are read off from the positions of the three arcs in the six thyatrons *AB*, *CD* and *EF*. Arcs in *B*, *D* and *F* respectively denote 1, 2 and 4, and in *A*, *C* and *E*, 0. By the use of two mechanical meters the multiples of 8 relating to the two sets of experimental conditions can be permanently recorded; but numbers between 0 and 7, i.e. the uncompleted eights, since they are represented only as arc-combinations, would be lost during a change-over, unless they could be recorded and remembered by some device. This is effected by means of two relay memories.

The general scheme consists in arranging three groups of relays as follows: (1) a group, called the "control" group, whose functions are (i) to carry out in correct sequence the nine operations involved in the change-over from one experimental condition to the other on receipt of an impulse from a clock every 10th sec., and (ii) to restart the counting process exactly 1 sec. later; (2) two other groups, called "memory *A*" and "memory *B*," associated with the thyatron counter and interconnected with the control group, which come into operation alternately. When operated by the control group, these latter serve to record the positions of the thyatron arcs, to remember the reading for 10 sec., and subsequently to reset the thyatron counter to this position so as to continue with the count. In this way, at a change-over, the combination of arcs at the end of an *A* counting-period is remembered by the *A* memory. In the meantime the thyatron counter is being used for a *B* count. At the next change-over, the *B* memory records and remembers the positions of the arcs at the end of the *B* counting period, while the *A* memory restores the arcs to the positions they occupied at the end of the preceding *A* count

* C. E. Wynn-Williams, *Proc. R.S. A* 136. 312 (1932).

and so enables them to continue to count from this point under experimental condition *A*, and *vice versa*.

The arrangement used is shown in the two figures. Figure 1 illustrates the general principle, while figure 2 shows the relay circuits. In figure 1, for simplicity, only the anodes and the grids of the thyatrons are shown, the rest of the counter circuit being exactly as illustrated in figure 5 of the original paper on the scale-of-two counter*.

§ 2. MODE OF OPERATION

In each of the memory groups, three relays, 1*a*, 2*a* and 4*a*, and 1*b*, 2*b* and 4*b*, figure 1, are associated with the three thyatrons *B*, *D* and *F*, which, when in the arcing condition, indicate respectively that 1, 2 and 4 are to be added to the meter reading. When the in relay 1*a* or 1*b* of a memory group is operated, these three relays are momentarily connected to the anodes of their associated thyatrons. If there are arcs in any of these thyatrons the corresponding relays are operated and locked, so as to record and remember the state of the thyatrons, i.e. the

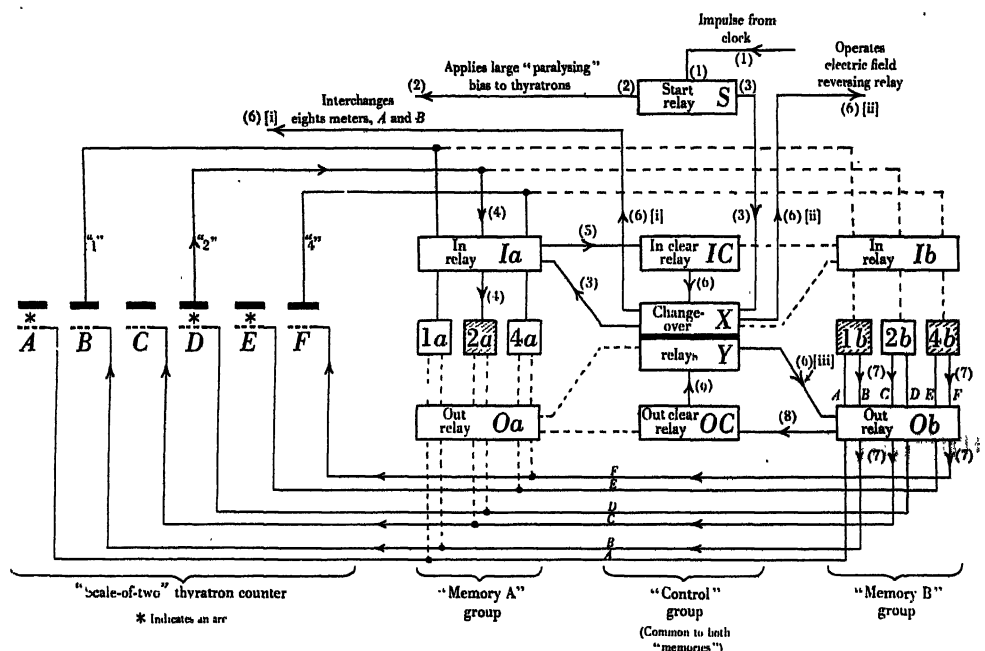


Figure 1. Memory *A* shown recording 2 from thyatron *D*; as soon as this is completed, control group causes memory *B* (which had been remembering 5 as 1 + 0 + 4) to transfer the arcs to thyatrons *B*, *C* and *F*, corresponding to 5. The numbers opposite the arrows correspond to those of the accompanying programme of events.

positions of the arcs. When the out relay *Oa* or *Ob* is operated, on the other hand, a large positive impulse is sent along three of the six wires attached to the six thyatron grids, so as to bring the arcs from whatever position they occupy to a new

* *Loc. cit.*

starting position, which is identical with some previous stopping position which had been recorded and remembered by the 1, 2 and 4 relays of either memory. The decision as to which grid of each of the three pairs of thyratrons *AB*, *CD*, *EF* receives the impulse, is governed by the state of the associated relay; for example, if the 2 relay is locked, *D* receives the impulse, and if it is unlocked, *C*.

The control group consists of six relays, a start relay *S*, a pair of change-over relays *X* and *Y*, an in clear relay *IC*, an out clear relay *OC*, and a meter-guard relay *G* (not shown in figure 1). The function of these relays is to bring about the required alternations of the experimental conditions every 10 sec. Conditions are reversed by relays *X* and *Y*. Condition *A* is maintained by *X* and *Y* remaining unlocked during the 9-sec. counting-period, while condition *B* is maintained by *X* and *Y* remaining locked during the period.

The following programme of events indicated by the lines and numbered arrows of figure 1, taken in the order set out, will make the mode of operation clear. Assume that a count is in progress under experimental condition *A*, with a positive potential on the source.

At the tenth second. (1) A clock impulse operates the start relay *S*. (2) The thyratrons are rendered inoperative by the application of a large negative grid bias. Suppose that the arcs are in thyratrons *A*, *D* and *E*, corresponding to 2, when counting ceases. (3) An impulse is sent via relay *X* of the control group, to the in relay, *Ia* of memory *A*. (4) The in relay *Ia* momentarily connects relays 1*a*, 2*a* and 4*a* of memory *A* to the thyatron anodes. Relay 2*a* locks, but not 1*a* or 4*a* as there are no arcs in thyratrons *B* and *F*. (5) The in relay *Ia* signals the end of the recording operation by operating the in clear relay *IC* of the control group. (6) The in clear relay causes one of the change-over relays *X* to lock. This causes [i] eights meter *B* to be substituted for meter *A*, [ii] a relay (not shown) to reverse connexions to the 10,000 V. potential-supply; [iii] an impulse to be sent to the out relay *Ob* of the *other* memory group *B*. (7) The out relay *Ob* causes positive impulses to be sent along three grid wires, the selection of which depends on which of the 1*b*, 2*b* and 4*b* relays had been locked during the previous change-over. Suppose these were 1*b* and 4*b*; then the arcs are transferred from positions *A*, *D* and *E* to positions *B*, *C* and *F*. (Later on, at the eleventh second, relays 1*b* and 4*b* are unlocked, so as to forget, as they have now served their purpose for the time being.) (8) The out relay *Ob* signals the end of the restoring process by operating the out clear relay *OC* of the control group. (9) The out clear relay *OC* causes the other change-over relay *Y* to lock, preventing further relay movements.

All the above operations (1) to (9) are carried out in rapid succession in less than half a second.

At the eleventh second. The start relay *S* is unlocked by the clock; the large negative bias applied to the thyratrons to paralyse them during the change-over is removed, and the count proceeds under experimental condition *B*, corresponding to a negative potential on the source, multiples of eight being now recorded on the eights meter *B*. This condition is maintained throughout the next 9 sec. by relays *X* and *Y* remaining locked during this period.

At the twentieth second. A change-over back to normal (condition *A*) takes place, the sequence of events being much as before but with the operations of the memory groups *A* and *B* interchanged. Operations (1) and (2) are as before. In (3), (4) and (5), on account of relays *X* and *Y* now being locked instead of free as before, an impulse is directed to the in relay *Ib* instead of *Ia*, and memory *B* therefore carries out the recording instead of memory *A*, as is indicated by the broken lines in figure 1. At (6) relay *X* is *unlocked*, reversing the experimental conditions from state *B* back to state *A*; and at (6) [iii], (7) and (8), on account of relay *Y* being locked, instead of unlocked as before, the out relay *Oa* of memory *A* is operated, causing memory *A* to carry out the restoring operation previously performed by memory *B*. At (9) relay *Y* is *unlocked*, and the count under condition *A* is resumed at the twenty-first second.

A cycle, of two 9-sec. counts under the two experimental conditions and two complete change-overs, has thus been completed in 20 sec. This process continues, and the total numbers of particles counted under the two sets of conditions are given finally on the dials of the two eight's meters*.

It might appear that this method of achieving the desired result is unnecessarily complicated†. It should, however, be emphasized that a system of interconnected relays such as this is capable of carrying out the complicated sequence of operations with precision in a far shorter time than could be done by any other electro-mechanical device and, in any case, in a fraction of the time required by a human observer. Moreover, the speed and precision of the operations do not fall off with time during a prolonged run.

§ 3. OPERATION OF RELAY CIRCUITS

The action of the relays in the previously described programme of events following the tenth second and numbered (1) to (9) will now be described in detail. The sectional numbers given below correspond to those of the previous programme, and the various circuit elements are designated by the letters (*a*) to (*h*) so that they may be easily traced in figure 2.

(1) *Circuit (a).* The clock closes and opens contact *P* every second, and *Q* every tenth second. At the tenth second, circuit of start relay *S* is completed via +, winding *S*, *Q* and -, and relay *S* is energized. All *S* contacts are operated. When *P* and *Q* subsequently open together, about half a second later, *S* is still kept in the operated state since it is locked via +, the other winding *S'*, resistance

* Of the two final uncompleted eights, one can be read directly from the final positions of the thyatron arcs, while the other is registered on one of the two memories and can be read from the relays themselves, or from the thyatron arcs by arranging a change-over.

† An experiment of this kind could, of course, be carried out by means of two separate thyatron counters, so that the relay memories *A* and *B* could be dispensed with. Even so, however, several relays would be required to effect the rapid change-over, and the inclusion of the memory groups entails far less complication than a second complete counter would. Further, the expense involved in the construction of the relay apparatus is far less than that of six additional thyatrons and their associated apparatus, and its useful life is much greater. Finally, it is always preferable to take sets of experimental observations with the same piece of apparatus when they have to be compared with one another.

$R.1$, $S.2$ and $-$. It remains in this state throughout the remaining stages. (2) *Circuit (e)*. $S.1$ closes before any other S contact, and applies a large negative potential across $R.2$ to increase the thyatron bias sufficiently to paralyse the counter, thus stopping the count and guarding the counter from surges. (3) *Circuit (a)*. The closing of $S.2$ completes the circuit of the in relay Ia , via $+$, $OC.1$, $Y.3$,

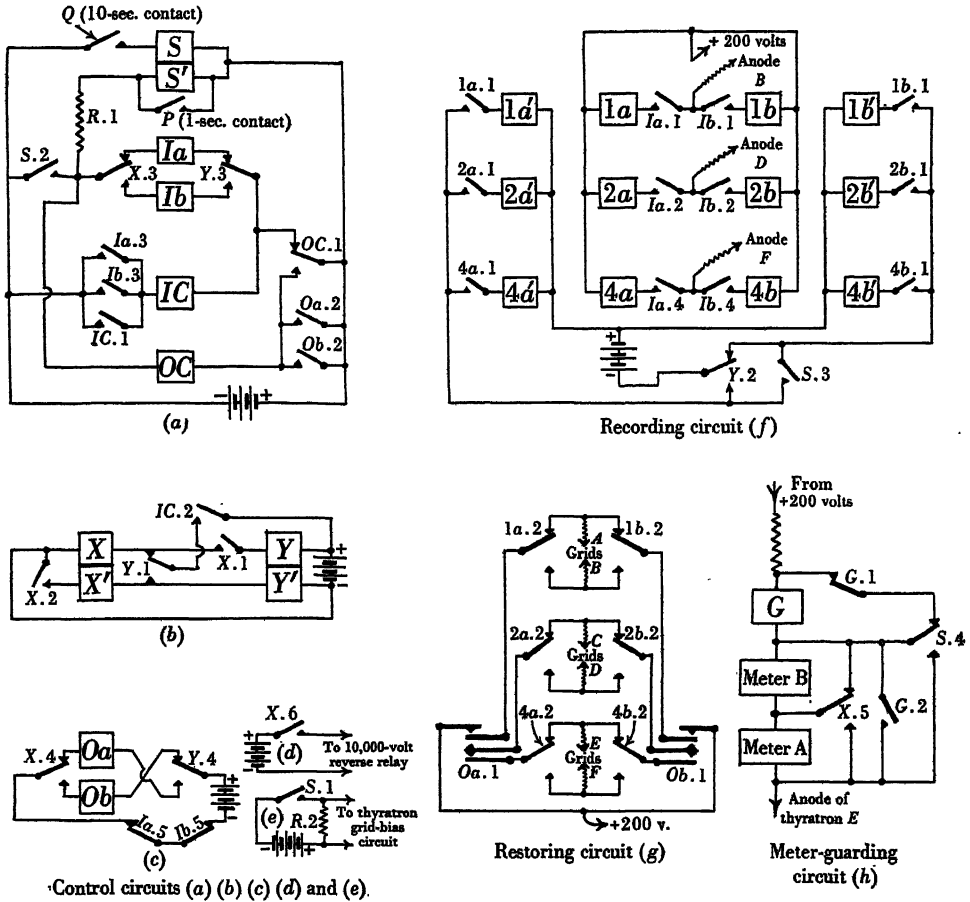


Figure 2*.

winding Ia , $X.3$, $S.2$ and $-$. Relay Ia is energized†. (4) *Circuit (f)*. Contacts $Ia.1$, $Ia.2$ and $Ia.4$ therefore close, and rather later, contact $Ia.3$ closes in circuit (a). The former complete the circuits of relays $1a$, $2a$ and $4a$. Suppose there is an arc in thyatron D ; relay $2a$ is energized via $+$ 200 V., winding $2a$, $Ia.2$, resistance,

* For simplicity, the usual convention of separating relays and their contacts has been adopted. It will be understood that when any relay, such as S , is actuated, all contacts designated by the relay letter, such as $S.1$, $S.2$, $S.3$ and $S.4$, operate, although they may appear in the figure in different circuits. When a relay has two windings the same letter is used for both; thus, windings S and S' both belong to relay S . A common battery suffices for all the circuits, but it is less confusing to show a separate battery for each.

† Note that had relays X and Y been locked prior to the change-over period, $X.3$ and $Y.3$ would have been down and Ib would have operated instead of Ia .

anode of thyatron *D*, arc and cathode. Relay *2a* is actuated, contact *2a.1* operates, and also contact *2a.2* in circuit (*g*). Relay *2a* is now locked independently of *Ia.2*, via the circuit +, the other winding *2a'*, *2a.1*, *S.3*, *Y.2* and —. (5) *Circuit (a)*. Late closing of *Ia.3* completes the circuit of the in clear relay via +, *OC.1*, winding *IC*, *Ia.3*, and —. Relay *IC* actuated, and contact *IC.1* now locks *IC* independently of *Ia.3*. (6) *Circuit (b)*. Closing of *IC.2* completes the circuit of relay *X* via +, *IC.2*, *Y.1*, winding *X*, and —. Relay *X* is actuated and all *X* contacts operate*, causing *in circuit (h)* operation of *X.5* to transfer the short-circuit from the eights meter *B* to meter *A*; *in circuit (d)* closure of contact *X.6* to energize a high-potential reversing relay, which reverses the connexions of the 10,000 V. supply; *in circuit (a)* operation of *X.3* to break the circuit of *Ia*, so that relay *Ia* and all *Ia* contacts return to normal; *in circuit (c)* operation of *X.4* to complete the circuit of out relay *Ob*† via +, *Y.4*, winding *Ob*, *X.4*, *Ia.5*, *Ib.5* and —, so that relay *Ob* actuated, and contacts *Ob.1* and *Ob.2* close, the latter rather later than the former; (7) *Circuit (g)*. The closing of *Ob.1* connects *1b.2*, *2b.2* and *4b.2* to + 200 V. Supposing relays *1b* and *4b* to be locked, contacts *1b.2* and *4b.2* would be down, and *2b.2* up; hence the grids of thyatrons *B*, *C* and *F* receive a positive potential, via the series resistances. The arcs are transferred to these thyatrons. (8) *Circuit (a)*. Late closing of *Ob.2* completes the circuit of the out clear relay *OC* via +, *Ob.2*, winding *OC*, *S.2*, and —. Relay *OC* is actuated and contact *OC.1* operates, locking relay *OC* independently of *Ob.2*, via +, *OC.1*, winding *OC*, *S.2*, and —; *OC.1* also breaks the circuit of relay *IC*, which now releases, and contacts *IC.1* and *IC.2* return to normal. (9) *Circuit (b)*. The opening of *IC.2* breaks the short-circuit across winding *Y*; relay *Y* operates in series with *X*, and both relays remain locked‡. In circuit (*c*), operation of *Y.4* breaks the circuit of out relay *Ob*, which releases; all *Ob* contacts return to normal, and positive potential is removed from the thyatron grids. In circuit (*f*), operation of *Y.2* maintains a locking circuit for relays *1a*, *2a* and *4a*, and arranges for the circuit of relays *1b*, *2b* and *4b* to be broken when *S.3* opens at the eleventh second; i.e. it arranges that memory *A* shall remember and memory *B* shall forget. At this stage, the apparatus waits for the start signal from the clock to arrive at the eleventh second.

At the eleventh second. Circuit (a). The clock closes *P*, but not *Q*. Winding *S'* is short-circuited by *P*, but the battery is protected by resistance *R.1*. Relay *S* now unlocks, and all *S* contacts return to normal. *S.2* releases the out clear relay *OC* in circuit (*a*). In circuit (*f*), *S.3* releases all the *B* memory relays, but the *A* memory relays are still locked via *Y.2*, which is now down. Finally§, in circuit (*e*), *S.1* removes the high grid bias, and the thyatrons begin counting.

During the next 9 sec. relays *X* and *Y* remain locked in series, all their contacts

* Note that relay *Y* is now in series with *X* via *X.1*, but cannot operate until subsequent opening of *IC.2*, at stage (9), breaks the short-circuit *X.1*, *Y.1*, *IC.2*, winding *Y*, and *X.1*.

† Note that (i) relay *Ob* cannot operate until *Ia.5* is right back to normal, indicating that the recording process is completed; and (ii) if *X* and *Y* were *locked* prior to the change-over, *X.4* and *Y.4* would have been down and *Oa* would have operated instead of *Ob* on the operation of *X.4*. Compare with the footnote to stage (3).

‡ See footnote to stage (6).

§ *S.1* is so adjusted as to close before and to open after the operation of *S.2*, *S.3* and *S.4*.

being in the operated state. At the twentieth second, *Ib* operates instead of *Ia*, and *Oa* instead of *Ob*, as has been mentioned in the footnotes to stages (3) and (6). At (6), closing of *IC.2* connects the other winding *X'* of relay *X* in parallel with winding *X*, via +, *IC.2*, *Y.1*, winding *X'*, *X.2*, and -; the magnetic field of windings *X* and *X'* neutralize one another and relay *X* releases, but relay *Y* is still locked via +, *IC.2*, *Y.1*, winding *Y'*, and -. At (9), the opening of *IC.2* breaks this circuit and relay *Y* unlocks, all *X* and *Y* contacts now having reverted to normal for the next count. Corresponding contacts in the two memory groups carry out similar operations during the alternate counts, and a similar cycle can be followed for events (1) to (9) with the letters *a* and *b* interchanged in the foregoing. It should be borne in mind that relays *X* and *Y* start this time by being *locked*.

Meter guard relay, circuit (h). The two eights meters are connected in series in the anode circuit of thyatron *E*, and one or other is normally rendered inoperative by being short-circuited by contact *X.5*. During a change-over the anode current of thyatron *E* may suffer interruption, which would cause spurious eights to be recorded; this is prevented by arranging that both meters shall be short-circuited, by the operation of *S.4*, during the whole of the change-over process. If, however, there is an arc in thyatron *E* when *S.4* subsequently returns to normal, one meter will immediately score a spurious eight. To prevent this, a guard relay *G*, which is normally short-circuited by *G.1* and *S.4* in series, is employed. When *S.4* is operated the short-circuit is broken, and if there is an arc in thyatron *E* relay *G* is energized and places an additional short-circuit across the two meters via *G.2*; it also breaks its own short-circuit at *G.1*. After the return of *S.4* to normal at the commencement of a counting-period both meters are still short-circuited by *G.2*; at some stage, the arc moves from thyatron *E* to thyatron *F* causing relay *G* to release and re-short-circuit itself at *G.1*, and to render one meter operative by the opening of *G.2*. This state continues during the rest of the counting-period. Thus relay *G* diverts an initial spurious eight impulse away from the meters.

MAGNETIZED ELLIPSOIDS AND SHELLS IN A PERMEABLE MEDIUM

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ABSTRACT. The relation between the magnetic fields round a uniformly magnetized ellipsoid when in a vacuum and when immersed in a permeable medium is investigated. The probability that the field round a thin normally magnetized shell is independent of the permeability of the medium surrounding it is discussed.

IT has been shown in a former communication* that if the magnetic force at an external point due to a uniformly magnetized sphere surrounded by a medium of constant relative permeability μ is compared with the magnetic force due to a sphere of the same radius and magnetization surrounded by a vacuum, the forces at corresponding points throughout the field will correspond in direction and be proportional in magnitude. For spheres the ratio of the forces was shown to be $3/(2\mu + 1)$.

More recently, this result has been extended by Prof. Leigh Page† to the case of a spheroid uniformly magnetized parallel to its axis of symmetry, and the ratio of the forces has been determined as a function of the eccentricity of the spheroid. It has become of interest, therefore, to inquire whether the same result is capable of still further extension, and if so with what limitations, if any.

It is easy to show that the result holds good for the case of a body with uniform magnetization I and of such a shape that the demagnetizing force within it due to its magnetization is uniform and collinear with I and so may be denoted by $-\lambda I$.

If such a body is surrounded by a vacuum the magnetic force at either an external or an internal point is well known to be that due to a surface distribution $+I \cos \theta$, where θ is the angle between the positive directions of I and of an outward-drawn normal.

If the body is surrounded by a medium of constant relative permeability μ we shall proceed to show that the magnetization produced in this medium will give rise to the same magnetic force as a surface distribution of density $-\alpha I \cos \theta$, where α has a suitable constant value. For on this assumption the magnetic force in the positive direction of I at an internal point will be $-\lambda I(1 - \alpha)$ and at a point just inside the surface of the body this can be resolved into $-\lambda I(1 - \alpha) \sin \theta$ tangentially and $-\lambda I(1 - \alpha) \cos \theta$ normally outwards. At an adjacent point in

* *Proc. Phys. Soc.* 45, 82 (1933).

† *Phys. Rev.* 44, 112 (1933).

the medium, while the tangential force is unaltered, the two surface distributions $+I \cos \theta$ and $-\alpha I \cos \theta$ increase the normal outward force by $4\pi I \cos \theta$ and $-4\pi\alpha I \cos \theta$ respectively, and it thus becomes $I(1 - \alpha) \cos \theta (4\pi - \lambda)$. The boundary conditions which must be satisfied are that at the surface of separation the tangential components of the internal and external magnetic force and the normal components of the internal and external magnetic induction shall be respectively equal. Of these, the former is satisfied identically. As to the latter, since the magnetic induction within the body is the sum of $4\pi I$ and the magnetic force $-\lambda I(1 - \alpha)$, its normal component is $I \cos \theta [4\pi - \lambda(1 - \alpha)]$, and since the normal component at a point in the medium is the product of μ and the normal magnetic force, it follows that

$$I \cos \theta [4\pi - \lambda(1 - \alpha)] = \mu I \cos \theta (1 - \alpha) (4\pi - \lambda).$$

This is satisfied for all values of θ if $4\pi - \lambda(1 - \alpha) = \mu(1 - \alpha)(4\pi - \lambda)$ and hence our assumption is justified and the value of α is given by

$$1 - \alpha = 4\pi / (4\pi\mu - \mu\lambda + \lambda), \text{ or } \alpha = (\mu - 1)(4\pi - \lambda) / (4\pi\mu - \mu\lambda + \lambda).$$

The second boundary condition may also be obtained, as in the case of a sphere*, by equating the surface density $-\alpha I \cos \theta$ due to the magnetization of the medium and the product of the susceptibility κ and the normal inward magnetic force in the medium. Thus

$$-\alpha I \cos \theta = -\kappa I \cos \theta (4\pi - \lambda)(1 - \alpha), \text{ or } \alpha / (1 - \alpha) = \kappa (4\pi - \lambda).$$

Remembering that $\kappa = (\mu - 1)/4\pi$, this gives the same value for α as before.

We may note, again as in the case of a sphere, that the induction within the body is given by $4\pi I - \lambda I$ if the body is in a vacuum and by $4\pi I - \lambda(1 - \alpha)I$ if the body is surrounded by the medium. It is clear that the ratio of the latter to the former must be the product of μ and the constant ratio of the magnetic forces at corresponding points in the latter and the former case. Thus

$$\mu(1 - \alpha) = (4\pi I - \lambda I + \alpha\lambda I) / (4\pi I - \lambda I),$$

which again leads to the same value of α .

Following the notation employed by Page, let γ be the ratio of the field-strength for a vacuum to that for the medium, and let r be the quotient $(\gamma - 1)/(\mu - 1)$. Then

$$\gamma = 1 / (1 - \alpha) = \mu - (\mu - 1)\lambda / 4\pi$$

and

$$r = 1 - \lambda / 4\pi.$$

Now it has been pointed out by Maxwell† that the most general form for a body in which uniform magnetization produces uniform demagnetizing force is an ellipsoid, and further that if the demagnetizing force is collinear with the magnetization their direction must be that of one of the axes.

Let a, b, c be the axes of the ellipsoid. Then if the magnetization is along the axis a the corresponding value of λ , which we may denote by λ_1 , is†

$$2\pi abc \int_0^\infty \frac{du}{(a^2 + u)\sqrt{(a^2 + u)(b^2 + u)(c^2 + u)}}.$$

* L. R. Wilberforce, *loc. cit.*

† *Electricity and Magnetism*, 2, 67-9 (3rd edition).

If the ellipsoid is now surrounded by a medium of permeability μ , the lines of force in the medium will be identical with those in the vacuum which it replaces, but the magnetic force at each point will be divided by $\mu - (\mu - 1) \lambda_1/4\pi$. This is equivalent to the statement that the magnetic field in the medium due to an ellipsoid with magnetization I along the axis a is the same as that in a vacuum due to the same ellipsoid with magnetization $I/[\mu - (\mu - 1) \lambda_1/4\pi]$ along the same axis.

Similar results follow if the ellipsoid is magnetized along the axis b or the axis c , the quantity λ_1 being replaced by λ_2 in the one case and λ_3 in the other, where

$$\lambda_2 = \int_0^\infty \frac{du}{(b^2 + u) \sqrt{(a^2 + u)(b^2 + u)(c^2 + u)}}$$

and

$$\lambda_3 = \int_0^\infty \frac{du}{(c^2 + u) \sqrt{(a^2 + u)(b^2 + u)(c^2 + u)}}.$$

It follows that if the ellipsoid is uniformly magnetized with intensity I but non-axially, so that the direction cosines of I referred to the axes are l, m, n and if it is surrounded by the medium, the resultant field will be the same as that in a vacuum due to an ellipsoid of the same dimensions but so magnetized that its axial components are

$$Il/[\mu - (\mu - 1) \lambda_1/4\pi], \quad Im/[\mu - (\mu - 1) \lambda_2/4\pi], \quad In/[\mu - (\mu - 1) \lambda_3/4\pi].$$

This resultant magnetization is of course uniform, but it differs in direction from that of the original ellipsoid; thus the two fields no longer correspond in direction and therefore cease to be everywhere proportional in magnitude. Hence the solution for this comparatively simple case does not bear out Page's generalization that "the effect of immersing a permanently magnetized body of any shape in a magnetic medium of constant permeability is to reduce the field everywhere in the same ratio, this ratio being a function of the permeability of the medium and of the geometrical configuration of the body alone."

For a prolate spheroid of eccentricity e magnetized along the axis of revolution

$$\lambda = 4\pi \frac{1 - e^2}{e^2} \left(\frac{1}{2e} \log \frac{1 + e}{1 - e} - 1 \right)$$

and for an oblate spheroid

$$\lambda = 4\pi \left[\frac{1}{e^2} - \frac{\sqrt{(1 - e^2)}}{e^3} \sin^{-1} e \right]^*.$$

Thus r , which is $1 - \lambda/4\pi$, becomes for the former

$$\frac{1}{e^2} \left[1 - \frac{1 - e^2}{2e} \log \frac{1 + e}{1 - e} \right]$$

and for the latter

$$\frac{1}{e^2} \left[e^2 - 1 + \frac{\sqrt{(1 - e^2)}}{e} \sin^{-1} e \right].$$

* Maxwell, *loc. cit.*

These agree with Page's results, since $\cot^{-1}[\sqrt{(1-e^2)}/e] = \sin^{-1}e$.

For spheroids magnetized perpendicularly to the axis of revolution, if prolate

$$\lambda = \frac{2\pi}{e^2} \left[1 - \frac{1-e^2}{2e} \log \frac{1+e}{1-e} \right]$$

and if oblate

$$\lambda = 2\pi \frac{\sqrt{(1-e^2)}}{e^2} \left[\frac{1}{e} \sin^{-1}e - \sqrt{(1-e^2)} \right]^*$$

while it is easily shown that for elliptic cylinders magnetized transversely in the direction of the major axis

$$\lambda = 4\pi \frac{\sqrt{(1-e^2)}}{1 + \sqrt{(1-e^2)}},$$

and in the direction of the minor axis

$$\lambda = 4\pi \frac{1}{1 + \sqrt{(1-e^2)}}.$$

The ratios of reduction of the magnetic field due to the surrounding medium may thus be readily calculated for these various cases.

In considering the effect of a surrounding medium upon the demagnetizing field and hence upon the magnetic induction in a spheroid so prolate that it approximates to a needle or so oblate that it approximates to a disc, Page has overlooked the fact that in the former case the demagnetizing force is negligible compared with the magnetization and therefore its diminution in a finite ratio does not sensibly increase the induction, while in the latter case although the change of the demagnetizing force is a very small fraction of its former value this change considerably affects the induction, which is the difference between $4\pi I$ and a nearly equal demagnetizing force.

It is obvious, in fact, that in the former case, since the field in the medium has $1/\mu$ of its value in a vacuum, the induction in the medium, and hence that in the needle, is unaltered, while in the latter case, since the field in the medium is the same as that in a vacuum, the induction in the medium, and hence that in the disc, is increased μ -fold.

The latter result can be verified as follows. Let the value of e for an approximate disc be $(1-\delta)$ where δ is small, then the corresponding value of λ becomes $4\pi - 2\sqrt{2} \cdot \pi^2 \sqrt{\delta}$ and that of α becomes $(\mu-1) 2\sqrt{2} \cdot \pi^2 \sqrt{\delta}/4\pi$, if we neglect in each case higher powers of $\sqrt{\delta}$. The induction $(4\pi - \lambda) I$ when the disc is in a vacuum becomes $2\sqrt{2} \cdot \pi^2 I \sqrt{\delta}$ and the induction $[4\pi - (1-\alpha)\lambda] I$, when the disc is in the medium, becomes $2\sqrt{2} \cdot \pi^2 \mu I \sqrt{\delta}$.

In the case of the disc, which is the limiting form of the uniformly magnetized oblate spheroid, the external magnetic force at its surface is constant from the centre to the very edge, as is evident from the fact that both the magnetization and the demagnetizing forces in it are constant. Its field therefore differs altogether from that of a simple magnetic shell, in which the force changes rapidly as the edge is approached and ultimately becomes very large. For the spheroidal disc, with its

* Maxwell, *loc. cit.*

constant finite external field, the induced magnetization in a surrounding medium will be everywhere finite, and as the distance separating the equal positive and negative surface distributions due to this magnetization is infinitesimal, being the thickness of the disc, it follows that the magnetic force in the medium due to the joint effect of these two distributions will vanish.

This argument accounts for the interesting result established by Page, that the permeability of the medium in which the disc is immersed has no effect at all on the field, but it casts grave doubt upon the legitimacy of the extension by mere analogy of this statement to the case of the simple magnetic shell, in which the magnetic force and consequent magnetization increase indefinitely in the neighbourhood of the edge. That the result still holds good, however, at least in a case readily amenable to calculation, namely that of a semi-infinite plane shell with a straight line as boundary, can be demonstrated as follows.

If a quantity of magnetism uniformly distributed along an infinite straight line with a density $+\rho$ per unit length is considered, the magnetic force at a point whose distance from the line is r will be a repulsion $2\rho/r$. Hence, if we next consider a semi-infinite plane with a straight boundary and a surface density of magnetism $-\sigma$, and a point P whose perpendicular distance PN from the plane is t , where N is a point of the plane distant a from the edge, the component, perpendicular to the plane, of the magnetic force at P due to a strip parallel to the edge and at a distance x from N will be an attraction $2\sigma t dx/(x^2 + t^2)$, and therefore the total component magnetic force perpendicular to the plane is given by

$$2\sigma t \int_0^\infty \frac{dx}{x^2 + t^2} + 2\sigma t \int_0^a \frac{dx}{x^2 + t^2},$$

which reduces to

$$\sigma \left(\pi + 2 \tan^{-1} \frac{a}{t} \right).$$

If now we consider a semi-infinite plane magnetic shell of thickness t and surface densities $\pm \sigma$, the component of the magnetic force perpendicular to the shell at a point just outside the positive surface and at a distance a from the edge will be the resultant of $2\pi\sigma$ outwards and $\sigma(\pi + 2 \tan^{-1} a/t)$ inwards and thus become $\sigma(\pi - 2 \tan^{-1} a/t)$ acting outwards.

When a is large compared with t we may take $\tan^{-1} a/t = \pi/2 - t/a$ and the expression for the component magnetic force assumes the well-known form $2\sigma t/a$.

If the shell is now surrounded by a magnetizable medium of constant susceptibility κ , the induced magnetism will produce additional surface densities over the positive and negative surfaces of the shell whose value will be

$$\mp \kappa \sigma (\pi - 2 \tan^{-1} a/t)$$

if this distribution does not change the value of the magnetic field round the shell.

We proceed to inquire whether this condition is satisfied. If we have two infinite parallel straight lines at a distance t apart and with linear densities of magnetism $\pm \rho$ per unit length the magnetic force at a point equidistant from the lines and at a distance x from their plane is easily seen to be $2\rho t/(x^2 + t^2/4)$, the

direction of the force being the intersection of a plane parallel to that of the lines and a plane perpendicular to them. Hence if we consider a point Q within the shell midway between its surfaces and at a distance l from its edge and divide the shell into strips of width dx distant $l - x$ from the edge of the shell, the magnetic force at Q due to the surface distributions $\mp \kappa \sigma (\pi - 2 \tan^{-1} a/t)$ will be

$$\int_{-\infty}^l dx \kappa \sigma \left[\pi - 2 \tan^{-1} \frac{l-x}{t} \right] \frac{2t}{x^2 + t^2/4}.$$

We can evaluate this integral by using sufficiently approximate formulae to replace the factor $\pi - 2 \tan^{-1} (l-x)/t$.

It may be shown that for values of $(l-x)/t$ between 0 and 1, and between 1 and 5, the respective empirical formulae $\pi t/(l+t-x)$ and $2.15 t/(l+0.37 t-x)$ are adequate, while when $(l-x)/t$ is greater than 5 the approximate form $2t/(l-x)$ may be employed.

Inserting these, noting that

$$\int \frac{dx}{(b-x)(x^2+c^2)} = \frac{1}{b^2+c^2} \left[\log \frac{\sqrt{(x^2+c^2)}}{b-x} + \frac{b}{c} \tan^{-1} \frac{x}{c} \right]$$

and assuming that t is small compared with l we shall obtain for the magnetic force at Q

$$\frac{4\kappa\sigma t^2}{l^2} (2l\pi/t - \log t + \log l - \log 5 - 2) + \frac{4.3 \kappa\sigma t^2}{l^2} \log 3.92 + \frac{2\kappa\pi\sigma t^2}{l^2} \log 2.$$

If we denote by ϕ the product σt , the strength of the shell, and assume it to be finite while t is infinitesimal, then since the limit of $t \log t$ is zero the above result reduces to $8\pi\kappa\phi/l$. As this is the product of 4π and $2\kappa\phi/l$, the value of the positive and negative surface densities in the immediate neighbourhood of Q due to the induced magnetization at the two sides of the shell, it follows that the magnetic force due to the joint effect of these surface densities at points in the medium just outside the shell will be zero, and therefore that it will be zero throughout the medium.

Thus the field round a semi-infinite thin simple plane magnetic shell with a straight boundary and of given strength is the same whether the shell is surrounded by a vacuum or by a magnetizable medium of constant permeability.

We have seen that in the case of any simple thin magnetic shell the induced magnetization very near its edge must bear the sole responsibility for a change in the field, if such a change exists, and we should therefore expect that curvature of the edge would be without influence if its radius were large compared with t . Thus it seems reasonable to conclude that the result obtained in the case of the semi-infinite plane shell is true for a thin simple shell of any shape.

If so, the result will also be true for any shell, not necessarily simple but everywhere thin and everywhere magnetized perpendicularly to its surface, for such a shell is resolvable into a suitable aggregate of simple shells.

A NEW METHOD OF DETERMINING THE MAGNETIC SUSCEPTIBILITIES OF GASES AND VAPOURS

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ABSTRACT. A new method of determining experimentally the magnetic susceptibilities of gases and vapours is described. Compensation is effected for the test bulbs, and the influence of surface condensation, if any, of gases and vapours can be allowed for and separately investigated. Electromagnetic retorsion is employed and the arrangement is rendered independent of small changes in the magnetizing current. The molar susceptibility of carbon dioxide was found to be $-(20.79 \pm 0.08) \times 10^{-6}$, showing good coincidence with the values of other investigators. The arrangement is being improved in several directions to give much greater accuracy. A systematic investigation of many gases and vapours will then be undertaken.

§ I. INTRODUCTION

A LARGE amount of work has been carried out* on the determination of the magnetic susceptibilities of gases, on account of the theoretical interest aroused by such measurements. The usual method is to suspend a small test body in a non-uniform field produced between the pole-pieces of an electromagnet. The suspension fibre is of phosphor-bronze or delicate quartz. The couple acting on the test body is determined either by noting the angle of twist at the lower end of the suspension, or the angle of retorsion which is necessary at the upper end to bring back the test body to its zero position. We are not aware of any other method employed to determine the angle of twist. The chief difficulties in such measurements are (i) the precise centring of the test body (see for example the elaborate precautions taken by Havens*); (ii) the strain effects in the retorsion method even in the most perfectly elastic fibres; (iii) the determination of the temperature in the neighbourhood of the test body; (iv) the great variations in the couple accompanying very small alterations in the magnetizing current; and (v) convection currents in the gases under examination, which disturb the positions of the light test bodies.

* For earlier work and detailed references see Havens, *Phys. Rev.* 43, 992 (1933). Havens's results were published when we had already developed our method and taken down some measurements.

In the new method, our aim has been to avoid or correct for these various sources of error. Though our method is still being improved in several directions, we feel it advisable at this stage to publish the developments so far effected.

§ 2. EXPERIMENT

The magnetic field. The pole-pieces were cylindrical, having faces of diameter 8 cm. They were placed at a distance of 4 cm. from each other. To distort the magnetic field, two cylinders of good soft iron 7.5 cm. \times 2 cm. were placed vertically as in figure 1 and held in position by a wooden block which was fixed tightly between the pole-pieces.

The test body. Thin sealed tubes A_1 and A_2 , 12 mm. in diameter and 10 cm. long, were taken as the test bodies. Two other similar tubes C_1 and C_2 of exactly the same dimensions, but left open, acted as the compensating tubes. The four were bound together to form a rigid system and were carried on a central narrow tube of glass.

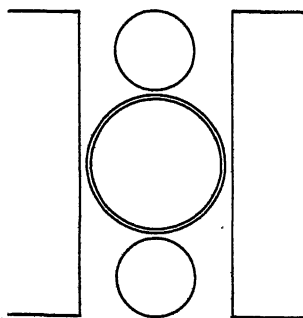


Figure 1.

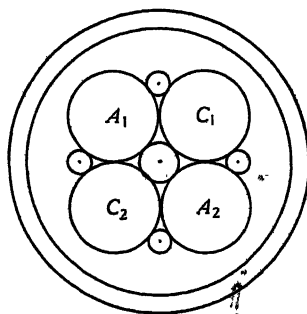


Figure 2.

The system weighed in all 34.71 gm. It was suspended by a fine platinum strip* of length 42 cm. and section $200\mu \times 50\mu$ in the distorted magnetic field with A_1A_2 making 45° with the pole-pieces as shown in figure 2. The forces acting on the tubes A_1 and A_2 are approximately perpendicular to A_1A_2 and produce a twist in the suspension. A mirror attached to the central tube serves to measure the twist in conjunction with a lamp and scale.

Electromagnetic retorsion. A null method was effected by compensating the magnetic couple acting on the test object with an electromagnetic one. The suspension was connected to a coil comprising a single turn of platinum wire wound about the tubes. This coil terminated in a small thick platinum wire dipping vertically into some mercury below. The plane of the coil in the null position was arranged to be normal to the pole-faces. During the magnetic experiments, the current passing through it in the proper direction would give an opposing couple and this current could be arranged to bring back the coil, and hence the test body, to the initial position.

* We now find that a bifilar suspension is preferable and introduces fewer complications with increased sensitiveness.

The optical arrangement. The whole system was enclosed in a long wide glass tube through the top of which the suspension wire of platinum was sealed. A bulge blown carefully on the tube facilitated observation of the deflections of the mirror. A convex lens of long focal length was used to compensate for the refraction of this bulge. The image of the cross-wire was focused on a photographically reduced scale of $\frac{1}{10}$ mm. and observed with a low-power microscope.

§ 3. THE THEORY OF THE COMPENSATING METHOD

We can show by a rigorous calculation that if the glass of the test body is correctly compensated, the unbalanced couple on the system becomes

$$\iiint \frac{1}{2} \cdot \frac{dH^2}{d\theta} (k_a - k) dv_a \quad \dots\dots(1)$$

where k_a and k are the volume susceptibilities of the air in the test body and of the surrounding gas in question, H is the magnetic field, θ the angle of twist, and dv_a an element of volume, the integral being extended over the volumes of the air in the test body. We may consider all the other effects to be balanced out.

The couple on the compensating coil of wire is given by

$$i \int H r (\sin \theta) dl \quad \dots\dots(2)$$

where i is the compensating current in the coil of platinum wire, r is the radius of the coil of which dl is an element of length, and the line integral is taken along the circuit.

For a given geometric arrangement of iron, the field at any point is given by $H = f(k, \mu) I$, where $f(k, \mu)$ is some function depending upon the geometry of the disposition and the permeability μ of the soft iron, and I is the current in the field coils. If the current is kept approximately constant, it can be assumed that this function at any point would remain constant. If this constant is taken as C , the expression (1) can be written as

$$I^2 \iiint \frac{1}{2} \cdot \frac{dC^2}{d\theta} (k_a - k) dv_a \quad \dots\dots(3),$$

or

$$I^2 (k_a - k) K \quad \dots\dots(4)$$

for any setting. The electromagnetic couple in (2) will become

$$i I \int C_1 r (\sin \theta) dl \quad \dots\dots(5).$$

If the compensating current i is tapped as a definite fraction (r/K) of the magnetic current I by a potential-divider, and is hence taken to be rI/R , we obtain for the above

$$\frac{rI^2}{R} \int C_1 r (\sin \theta) dl \quad \dots\dots(6).$$

For the zero position of the coil this becomes prI^2l/R where p is a constant and l the effective length. The condition for zero torsion is therefore

$$prI^2l/R = I^2 (k_a - k) K \quad \dots\dots(7),$$

or

$$prl/R = (k_a - k) K \quad \dots\dots(8).$$

We thus see that if R , the resistance in the compensating coil circuit, is kept constant,

$$k_a - k \propto r \quad \dots\dots(9).$$

Any small want of balance in the test body will merely introduce on the left a constant additive term which will become ineffective in our method of calculating the results.

Equation (8) is seen to be independent of any variations in the magnetizing current. It is to be noted that the compensating current is acted on by a magnetic field very close to the field which causes the deflection of the tubes, so that the compensation is local and hence nearly independent of external disturbances or small local displacements.

§ 4. ELECTRICAL CONNEXIONS

The electrical connexions are shown diagrammatically in figure 3. The magnetizing current of 8 A. was taken from a 120-V. battery B and measured with a care-

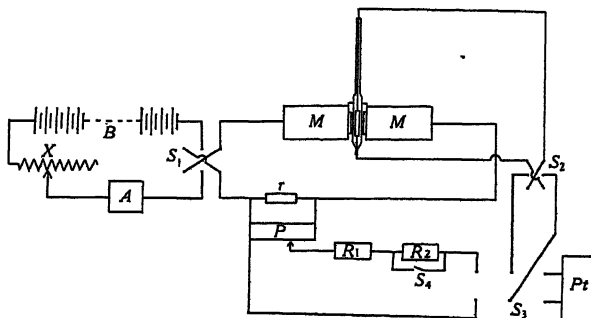


Figure 3.

fully calibrated ammeter A . S_1 is a commutator for reversing the current in the electromagnet M . The magnetizing current flows through a 0.1-ohm manganin resistance r of open type, which could be kept at a steady temperature by immersion in cold water. The potential at the ends of this low resistance served as the source of the compensation current. P is a potentiometer calibrated carefully to 0.1 per cent. It is of the Pye and Co.'s drum type with firm moving contact. R_1 is a resistance box and R_2 a single coil resistance of 100 ohms. The double-pole double-throw switch S_3 was made of six mercury cups in ebonite and amalgamated brass contact arms. The middle terminals were attached to the ends of the coil. The other two arms were connected to a platinum thermometer bridge Pt to indicate the mean temperature of the gas, the coil itself being used for the purpose. S_2 served for reversing the current in the coil for paramagnetic gases. S_4 was used in earlier experiments for short-circuiting the coil and served satisfactorily to control the oscillations of the system in the magnetic field. The null points were read with currents flowing in both directions. The residual field produced less than 0.1 per cent of the full-field deflection.

§ 5. READINGS WITH AIR AND CARBON DIOXIDE

By means of an elaborate system of glass connexions and a Cenco Hyvac pump, the experimental tube could be evacuated and flushed with pure dry air or gas repeatedly. The vacuum obtained was only a fraction of a millimetre. The pressures were read off on a mercury manometer open outside to the atmosphere, or at low pressures on a McLeod gauge. Air was passed over fresh soda lime and fused calcium chloride to free it from carbon dioxide and moisture. The carbon dioxide was generated by the action of pure dilute hydrochloric acid on marble, passed over glass wool dusted with pure sodium bicarbonate and then dried over fused calcium chloride. Check measurements with the platinum resistance thermometer bridge showed that the temperature inside did not vary by more than 0.05° .

Under proper conditions, the deflections for the gases were reproducible with a certainty of 1 in 1000 at pressures less than 50 cm. At higher pressures convection

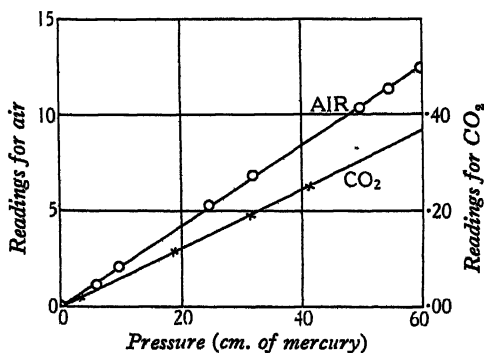


Figure 4.

currents gave small disturbances. We are now engaged in making some alterations in the apparatus which should bring down these disturbances to a minimum.

We have also recently introduced another coil of silver wire round the test body, so arranged that in the zero position the plane of this coil is nearly parallel to the pole-faces. This method of electromagnetic damping is very efficient and brings down the oscillations of the test body very rapidly.

In figure 4 are shown the curves between the pressure and the connected readings of the potentiometer. The corrections were arranged to be such that the deflection was zero when the pressure outside was the lowest obtainable. It will be seen that the points plot themselves on straight lines, thus presenting no Glaser anomalies. Havens obtained such anomalies even when the gases were dried on calcium chloride; but we have obtained no such variations. It is perhaps possible that continuous exposure of the chloride to the damp air increases the vapour pressure of the moisture in equilibrium with it.

Taking Sone's value of the volume susceptibility of air at normal temperature and pressure to be 0.0308×10^{-6} , we obtain for the volume susceptibility of carbon

dioxide the value -0.000928×10^{-6} . The molecular susceptibility becomes therefore 20.79×10^{-6} , which agrees well with the latest determination of

$$-(20.88 \pm 0.08) \times 10^{-6}$$

of Havens. It is believed that the error in our value is less than 0.4 per cent. Some preliminary experiments we have completed with benzene vapour indicate that this method is equally efficient for the study of the diamagnetic susceptibilities of vapours.

§ 6. ADVANTAGES OF THIS METHOD

We may here summarize the advantages of our method.

(i) Uncertainties in local fluctuations of densities due to temperature or pressure are rendered absent by making the test body sufficiently large in volume without increasing the weight. (ii) The magnetic field is definitely so distorted as to apply the maximum couple to the test body. (iii) The material of the container is adequately compensated. (iv) Proper facilities exist for separately studying and allowing for surface condensations. (v) Instead of mechanical retorsion, involving uncertainties even in the best experiments, we have here a method of electromagnetic retorsion applied to the body itself and not at the upper end. (vi) Since the current for the coil is tapped from the magnet circuit, small fluctuations of this current do not affect the equilibrium reading. (vii) The electromagnetic damping control on the test body makes easier the taking down of readings. (viii) A direct check on the inside temperature is possible by using the coil itself as a platinum resistance thermometer. (ix) Elaborate precautions for correct centring need not be taken, and the uncertainties on this account consequently disappear.

§ 7. ACKNOWLEDGMENT

We take this opportunity to thank the authorities of the Annamalai University for the award of a scholarship to one of us (G. Sivaramakrishnan) which has rendered this work possible.

DISCUSSION

Dr L. F. BATES. In Bitter's experiments on gases the test body used was a cylindrical glass vessel separated into four compartments or quadrants. Two opposite quadrants were evacuated and sealed, the others were open to the gas. Considerable skill in glass-blowing was obviously required in the manufacture of this test body. The authors have virtually used the same principle in their test body but they have shown that it can be constructed in a comparatively simple manner. It is interesting to note that apparently no surface-tension disturbances were observed at the platinum-mercury contact, and that the authors have designed a bifilar suspension which is more sensitive than a single torsion wire.

INTENSITY-DISTRIBUTIONS IN MOLECULAR SPECTRA: N_2 SECOND POSITIVE SYSTEM

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ABSTRACT. Intensities of bands in the $C^3\Pi \rightarrow B^3\Pi$ system of N_2 under four different conditions of excitation have been measured by means of calibrated photographs of the spectrum; transition probabilities derived from these have been compared with the Condon parabola as obtained from Morse's and Rydberg's potential-energy functions; effective temperatures have been derived on the assumption of a Boltzmann distribution for vibrational energy; and an attempt has been made to explain the variation of intensities and transition probabilities under some of the conditions studied.

§ 1. INTRODUCTORY

THE effect of temperature and excitation conditions on intensities within a band system has been but little investigated. The intensity changes due to pressure and influence of foreign gases have not been satisfactorily explained. In view of this, it is proposed to present in this paper accurate quantitative data on intensities of the second positive system of nitrogen produced under different experimental conditions and to study the results mainly from the standpoint of the Franck-Condon theory.

§ 2. EXPERIMENTAL

The intensity technique and photographic procedure adopted were precisely the same as those followed by Johnson and Tawde* on the C_2 Swan bands. On account of the extension of this system into ultra-violet region, a special ultra-violet-glass lamp capable of transmitting down to λ 2500 was procured from the General Electric Company Ltd. and calibrated with a quartz double monochromator in the usual way. The bands were photographed in two positions of the quartz prism on a Hilger E_1 instrument, the time for calibration marks and the spectrum being maintained equal by means of an automatic shutter. According to a suggestion made in the previously mentioned paper, slight fogging of plates preliminary to actual exposure was found to give satisfactory results.

The bands were excited in (i) the positive column of an ordinary end-on discharge tube; (ii) an uncondensed discharge in a mixture of 99 per cent of argon, 0.7 per cent of N_2 and 0.3 per cent of O_2 ; (iii) a high-frequency electrodeless discharge in air; and (iv) an uncondensed spark in air. It was also possible to produce

* *Proc. R.S. A* 137, 575 (1932).

these bands in the arc of a quartz pointolite lamp, but experiments in this connexion had to be given up owing to accidental breakage of the lamp filament. During all exposures, the conditions of experiment such as pressure, temperature, current etc. were maintained strictly constant. The photographic intensities have been corrected for the energy-distribution (E_λ, λ) of the standard lamp.

§ 3. RESULTS OF OBSERVATIONS

The results of intensities expressed on the scale of 1000 for the (0, 0) band have been recorded in tables 1 to 4. Immediately below the numbers denoting intensities are given the I/ν^4 values of the bands, ν being calculated from the following equation for the N_2 ($C^3\Pi \rightarrow B^3\Pi$) system*:

$$= 29653 \cdot 1 + (2018 \cdot 66 \nu' - 26 \cdot 047 \nu'^2) - (1718 \cdot 4 \nu'' - 14 \cdot 437 \nu''^2).$$

The excitation function $\Sigma I/\nu^4$ for each initial vibrational level has been calculated by taking the sum of the I/ν^4 values of the bands in each ν'' -progression. This is denoted in the first column of each table. Taking the I/ν^4 value for a band in each ν'' -progression and dividing it by the corresponding excitation function for that progression, we get a number proportional to the transition probability. These numbers are entered in ν' , ν'' schemes in figures 1 to 4.

With the aid of Morse's† potential-energy function, potential curves are drawn to scale in figure 5 for the $C^3\Pi$ and $B^3\Pi$ states of N_2 , the constants used being as follows:

$$C^3\Pi: D_e' = 40087; a' = 3 \cdot 2973; r_e' = 1 \cdot 14 \text{ \AA}.$$

$$B^3\Pi: D_e'' = 51995; a'' = 2 \cdot 4548; r_e'' = 1 \cdot 201 \text{ \AA}.$$

From these curves the parabola of maximum transition probabilities has been derived by the graphical method of Condon. It has been denoted by the letter M in figures 1 to 4.

In place of that of Morse, Rydberg‡ has recently given a modified potential-energy function of the following form:

$$U(r) = D_e(ax + 1)e^{-ax},$$

where

$$a = \sqrt{\frac{\mu(0 \cdot 1735 \omega_e)^2}{D_e}}$$

and

$$x = (r - r_e).$$

The constants used for N_2 in the above formula are:

$$D_e' = 40087; a' = 3 \cdot 3148; r' = 1 \cdot 14.$$

$$D_e'' = 51995; a'' = 2 \cdot 4666; r'' = 1 \cdot 201.$$

The resulting curves are plotted to scale in figure 6, except that the separation of the two scales used is arbitrary. The Condon parabola derived from these is shown by the letter R in figures 1 to 4.

* W. Jevons, *Report on Band Spectra*, p. 76 (Physical Society, 1932).

† *Phys. Rev.* **34**, 57 (1929).

‡ *Z. f. Physik.* **73**, 376 (1931).

Table 1. I and I/ν^4 values. Positive column in air

$\Sigma I/\nu^4$	ν''/ν'	0	1	2	3	4	5	6	7	8	9	10	11
456.87	0	1000 129.33	968.7 158.75	578.8 121.47	155.1 42.14	12.3 4.39	1.43 0.68	0.16 0.11	—	—	—	—	—
297.40	1	841.5 83.9	121.8 15.16	268.4 42.03	453.5 90.49	214.5 54.89	25.2 8.39	4.84 2.12	0.70 0.41	—	—	—	—
192.24	2	202.1 15.87	451.5 43.69	102.4 12.30	134.7 20.24	247.1 46.87	163.8 39.63	30.9 9.66	7.89 3.21	1.43 0.77	—	—	—
139.60	3	365.7 23.09	293.4 22.55	201.1 18.96	198.7 23.11	3.22 0.46	85.5 16.22	89.9 20.67	35.7 10.49	8.21 3.12	1.88 0.93	—	—
64.28	4	—	—	217.1 16.43	105.1 9.67	151.4 17.11	4.76 0.66	12.0 2.09	35.2 7.72	25.98 7.23	6.51 2.32	1.88 0.87	0.29 0.18

Table 2. I and I/ν^4 values. Argon tube

$\Sigma I/\nu^4$	ν''/ν'	0	1	2	3	4	5	6	7	8	9	10
301.42	0	1000 129.33	622.8 102.06	235.4 49.39	60.8 16.52	9.3 3.31	1.7 0.81	—	—	—	—	—
168.39	1	992.9 98.99	174.5 2.17	147.6 23.12	138.5 27.53	43.8 11.21	12.5 4.16	2.76 1.21	—	—	—	—
82.26	2	296.2 23.27	348.9 33.77	8.9 1.07	33.17 4.98	49.4 9.37	24.8 5.99	9.92 3.09	1.76 0.72	—	—	—
45.40	3	—	333.3 25.62	100.6 9.48	13.27 1.54	6.35 0.92	13.53 2.46	14.11 3.24	4.88 1.43	1.88 0.71	—	—
16.89	4	—	—	177.8 13.41	0.0 0.0	7.6 0.86	4.37 0.60	3.32 0.58	2.28 0.50	2.13 0.59	0.99 0.35	—

Table 3. I and I/ν^4 values. High-frequency electrodeless discharge

$\Sigma I/\nu^4$	ν' \diagup ν'' \diagdown	0	1	2	3	4	5	6	7	8	9	10
299.89	0	1000 129.33	769.4 126.07	145.4 30.51	46.22 12.55	4.02 1.43	—	—	—	—	—	—
171.68	1	968.9 96.57	35.9 4.46	225.6 35.21	87.64 17.47	54.8 14.02	11.86 3.95	—	—	—	—	—
111.45	2	669.9 52.58	328.1 31.73	194.8 2.33	32.63 4.90	52.14 9.88	31.3 7.57	7.91 2.46	—	—	—	—
61.56	3	—	506.9 38.96	147.9 13.94	27.5 3.19	4.21 0.59	8.65 1.56	10.31 2.36	3.27 0.96	—	—	—
9.39	4	—	—	34.18 2.57	39.85 3.66	11.21 1.26	0.0 0.0	6.86 1.15	1.99 0.44	1.13 0.30	—	—

Table 4. I and I/ν^4 values. Spark in air

$\Sigma I/\nu^4$	ν' \diagup ν'' \diagdown	0	1	2	3	4	5	6	7	8	9	10
279.82	0	1000 129.33	546 89.47	218.4 45.75	45.1 12.26	6.6 2.35	1.4 0.66	—	—	—	—	—
197.88	1	1047 104.38	18.93 2.35	207.8 32.55	189.5 37.71	52.99 13.56	19.27 6.41	2.10 0.92	—	—	—	—
164.76	2	712.6 56.0	660.2 63.88	29.56 3.55	28.29 4.25	101.9 19.33	40.28 9.75	21.55 6.72	3.14 1.28	—	—	—
105.33	3	—	552.3 42.45	413* 39.0	41.73 4.85	18.9 2.73	34.96 6.35	22.71 5.22	11.79 3.46	3.36 1.27	—	—
64.73	4	—	—	398.6 30.06	271.0* 25.0	27.51 3.11	0.0 0.0	10.63 1.35	12.10 2.65	5.89 1.64	2.59 0.92	—

* Determined by extrapolation.

ν' \ ν''	0	1	2	3	4	5	6	7	8	9	10	11
0	.283	.347	.262	.092	.009	.0015	.0002					
1	.282	.051	.141	.304	.184	.028	.007	.0013				
2	.082	.227	.064	.105	.244	.206	.050	.016	.004			
3	.165	.161	.135	.165	.0033	.116	.148	.075	.023	.0066		
4	-	-	.256	.150	.266	.010	.032	.120	.112	.036	.013	.003

M *R* *R* *M*

Figure 1. Transition-probabilities: positive column in air.

ν' \ ν''	0	1	2	3	4	5	6	7	8	9	10
0	.3129	.339	.164	.055	.011	.0037					
1	.588	.0129	.132	.216	.067	.025	.0072				
2	.283	.41	.013	.060	.114	.073	.037	.0087			
3	-	.565	.209	.034	.020	.054	.071	.0315	.0156		
4	-	-	.796	0	.056	.035	.034	.029	.035	.0205	

M *R* *R* *M*

Figure 2. Transition-probabilities: argon tube.

ν' \ ν''	0	1	2	3	4	5	6	7	8	9	10
0	.431	.420	.102	.042	.0017						
1	.562	.026	.205	.1017	.081	.022					
2	.472	.285	.021	.044	.088	.068	.0221				
3	-	.633	.226	.052	.0095	.025	.038	.015			
4	-	-	.273	.389	.134	0	.122	.017	.032		

M *R* *R* *M*

Figure 3. Transition-probabilities: high-frequency electrodeless discharge.

ν' \ ν''	0	1	2	3	4	5	6	7	8	9	10
0	.166	.322	.165	.014	.0085	.0024					
1	.528	.0119	.161	.1905	.068	.0324	.0046				
2	.340	.388	.0216	.0238	.1174	.0592	.0408	.0078			
3	-	.4025	.380	.016	.0259	.0603	.0496	.0328	.012		
4	-	-	.165	.386	.0481	0	.0208	.041	.0353	.0142	

M *R* *R* *M*

Figure 4. Transition-probabilities: spark in air.

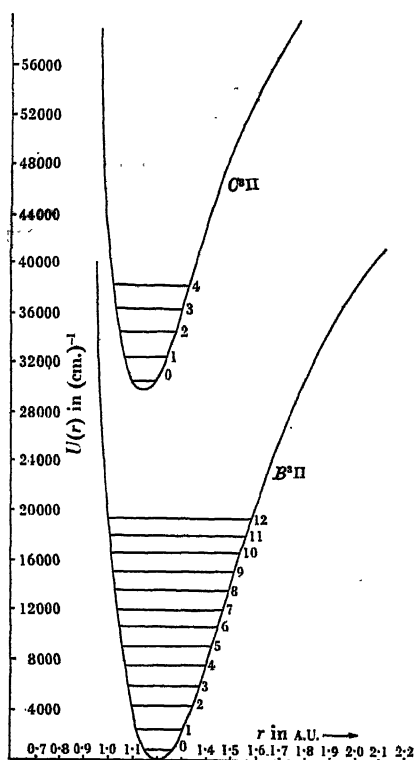


Figure 5. Potential curves for N_2 by Morse's function.

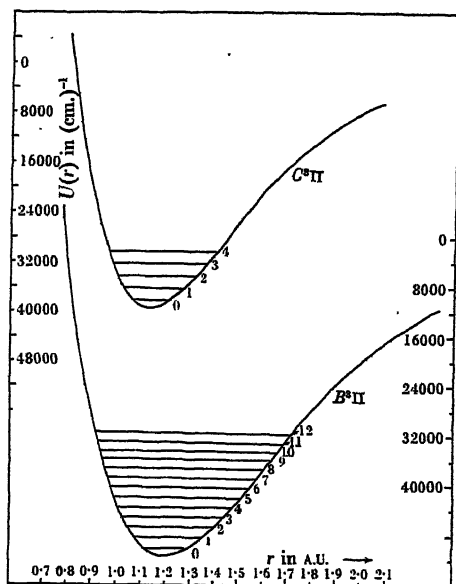


Figure 6. Potential curves for N_2 by Rydberg's function.

§ 4. EFFECTIVE TEMPERATURES

On the assumption that the number of molecules in each initial vibrational level are in thermal equilibrium at the temperature of the source, we should get

$$hc [\omega_e' (v' + \frac{1}{2}) - x_e' \omega_e' (v' + \frac{1}{2})^2] = kT \log_e (N_0/N).$$

Substituting the various constants for the upper $C^3\Pi$ state of N_2 , and converting N_0 to $N_{\frac{1}{2}}$, we get

$$2044.7 v' - 26.047 v' (v' + 1) = 1.6083 T \log_{10} (N_{\frac{1}{2}}/N_{v'+\frac{1}{2}}).$$

The numbers $N_{\frac{1}{2}}$ and $N_{(v'+\frac{1}{2})}$ are proportional to the excitation functions $\Sigma I/\nu^4$ in the respective initial vibrational levels. By plotting the logarithm of these ratios against the vibrational energy calculated from the left-hand side of the above equation, we get the absolute temperatures directly. The effective temperatures thus derived are:

- (i) Positive column in air: 6730° K.
- (ii) Argon-nitrogen mixture: 4670° K.
- (iii) High-frequency electrodeless discharge: 5400° K.
- (iv) Spark in air: 8420° K.

§ 5. CONCLUSIONS AND DISCUSSION

It appears from the results that the values of the relative intensities differ greatly from one excitation condition to the other. The intensities in table 1, relating to the positive column in air, are rather characteristic in the sense that, in contrast to what occurs in the case of the other conditions of excitation, the sequences corresponding to large change of quantum number are easily observable. On the other hand, the distribution in the high-frequency discharge is much nearer to that of excitation in high-pressure argon. It may be noted, however, that in all the cases studied there is a rise and fall of intensities along progressions such as is found for a normal band spectrum. The selective intensity of leading bands in sequences in the case of excitation in high-pressure argon makes it apparent that the effect observed is similar to one found by Johnson* in the first positive bands.

In connexion with the values of the intensities, a brief reference to the recent results of Okubo and Hamada† seems imperative. Those authors conclude that the lower the temperature of gas the better defined and sharper is the selective enhancement of bands with initial levels $v' = 0$ and $v'' = 1$. At higher temperatures the selective enhancement shifts to bands with quantum numbers greater than 0 and 1. In our results, only the bands (1, 0), (2, 0), (3, 1) are relatively more intense in high-pressure argon than in the positive column in air. This makes it apparent that it may not be the temperature effect that is alone responsible, as suggested by Okubo and Hamada, for the selective enhancement. Probably the change might be characteristic of the influence of inert gases. On the other hand, the examination of intensities in tables 3 and 4 shows that the bands (2, 0), (2, 1), (2, 2), (2, 4), (2, 5), (2, 6), (2, 7), (3, 1), (3, 3), (3, 4), (3, 5) and so on, belonging to v' -progressions with v' greater than 0 and 1 in the case of the spark in air, are relatively more enhanced than those in high-frequency electrodeless discharge. For bands with v' equal to 0 and 1, the enhancement is not at all pronounced. On the contrary, many of the bands belonging to these progressions are weaker in spark than in high-frequency discharge. These results are, therefore, in good agreement with Okubo and Hamada's conclusions referred to above, as molecules in a spark discharge are expected to be in a high-temperature atmosphere in comparison with high-frequency conditions.

The test of Condon's theory can be sought in figures 1 to 4. Here the results have been examined in the light of Morse's and Rydberg's potential-energy functions. The parabola as derived from Morse's formula appears wider than the locus of experimental figures, but it seems permissible to state that within the limits of experimental error the agreement with theory appears quite satisfactory. It is, however, interesting to note that a far better agreement results from the use of Rydberg's $U(r)$ function as may be seen from parabola R in figures 1 to 4.

According to Kaplan‡ the sudden curtailing of initial levels above $v' = 4$ in this

* *Phil. Mag.* 48, 1069 (1924).

† *Phys. Rev.* 37, 1406 (1931).

‡ *Astrophys. J.* 78, 130 (1933).

system has been explained by assuming a third repulsive level due to the coming together of two metastable 3D atoms, the transitions to which take place according to the Franck-Condon principle. This Heitler-London level cuts the potential curve for the $C^3\Pi$ state of N_2 in the neighbourhood of $v' = 5$. As a result of this the usual transitions to normal levels are quenched. If again, as has been suggested by Kaplan, such a level is sensitive to conditions of excitation, it should be possible to account for the variation of intensity within the progressions observed in tables 1 to 4 as a variation of intensity of interaction with normal levels.

In figure 7 is illustrated the effect of conditions of excitation on transition-probabilities. The transition-probabilities, derived from three cases studied here, are shown as a function of final vibrational quantum number in a v'' -progression ($v' = 2$). The graph shows too high a probability for $v'' = 1$ in the case of excitation in high-pressure argon, in spite of the fact that a Heitler-London level due to the coming together of two 4S atoms is supposed to cut the r_{\max} part of

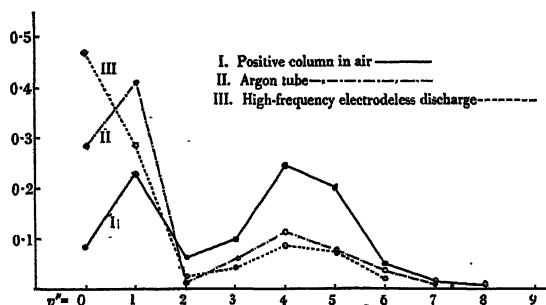


Figure 7. Transition-probabilities in v'' -progression ($v' = 2$).

the normal potential curve for the $B^3\Pi$ state of N_2 in the neighbourhood of this vibrational level. Normally the r_{\max} part of the Condon parabola as seen in figure 2 is considerably favoured relatively to r_{\min} by reason of the asymmetry of the $U(r)$ curves. This shows that argon does not favour the transition to the Heitler-London level. If, for example, it were assumed that the degree to which the Heitler-London level is favoured depends upon the concentration of appropriate metastable atoms in the neighbourhood of radiating molecules, we might expect the effect illustrated in figure 7 in the case of argon. With this assumption, it is reasonable to suppose that the excess of argon atoms breaks up the fields produced by metastable nitrogen atoms in the neighbourhood of radiating molecules.

As regards the effective temperatures, almost a linear relation has been obtained between the vibrational energy and $\log(N_0/N)$ on the assumption of a Boltzmann distribution; but the temperatures derived are nowhere near the real temperatures of sources, nor do they bear a simple ratio to them. But owing to the presence of only a few initial levels in this system, we cannot draw any definite conclusions regarding the populations of various levels being in statistical equilibrium with their surroundings. However, the evidence available points to the conclusion that a vibrational distribution does not hold.

§ 6. ACKNOWLEDGMENTS

I am indebted to Sir Robert Robertson, F.R.S., of the Government Chemical Laboratories, London, for permission to use the monochromator, to Prof. A. Fowler, F.R.S., for permission to use the micro-photometer of the Imperial College, and to the General Electric Company, Wembley, for supplying the special ultra-violet-glass lamp. I desire also to express my gratitude to Dr R. C. Johnson, under whose direction the work was carried out; and to the High Commissioner for India, for the award of a research grant which enabled me to complete it.

539.132:547.313.2

A NOTE ON THE TWISTING-FREQUENCY IN ETHYLENE

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ABSTRACT. From the experimental value for the fundamental twisting-frequency in ethylene, the magnitude of a certain carbon-carbon exchange integral J is determined as 0.72 ± 0.10 electron-volts. According to this result, the energy needed to twist one of the CH_2 groups through an angle $\pi/2$ with respect to the other about the C-C axis is 1.0 ± 0.2 . This agrees well with the experimental value for the heat of activation of dimethyl maleate to dimethyl fumarate.

§ 1. INTRODUCTION

IT has been known for some time from experimental evidence of several kinds⁽¹⁾ that the ethylene molecule is a plane one, but only recently was it possible to prove from quantum mechanics that this is the most stable configuration⁽²⁾. Intimately connected with the question of the stability of the molecule is the problem of calculating the amount of energy required to twist one of the CH_2 groups with respect to the other through an angle $\pi/2$ about the C-C axis. This quantity has been estimated very roughly at between $\frac{1}{2}$ and 1 electron-volt and it seemed impossible to get a more accurate value without tedious and difficult numerical calculation. We shall prove in the following note that a good estimate may be obtained from the observed fundamental twisting-frequency. In order to do this it is necessary to determine the force constant for small angles of twisting, a quantity which can be expressed very simply in terms of a certain fundamental exchange integral occurring in the theory of valency. Our problem resolves itself mainly into a determination of this integral.

Our calculations can be applied directly to ethane*. Here, however, there is very little resistance to twisting, as it is only the steric repulsions between hydrogen atoms in different CH_3 groups that hinder free rotation. Consequently, the fundamental twisting-frequency in ethane is very much less than in ethylene.

The ethylene molecule. On the assumption of perfect pairing of spins, the author⁽³⁾ has shown that if one CH_2 group is twisted from the equilibrium position through

* The various energy levels for rotations of the ethane molecule about the C-C axis have been very roughly evaluated by Teller and Weigert, *Gott. Nach.* p. 218 (1933), in connexion with the specific heat. A more exact determination does not seem to affect their results on the specific heat very much.

an angle ϕ with respect to the other, the change in potential energy is given with sufficient accuracy* by

$$V(\phi) = -\frac{3}{4}J \cos 2\phi \quad \dots\dots(1),$$

where J is a certain exchange integral, the exact equation for which is not needed for our present purpose. Equation (1) is a good approximation because the conditions in ethylene are very favourable to the assumption of perfect pairing. Moreover, there is no need to worry about Coulomb terms, as one usually has to do in this sort of calculation, because these do not give any dependence on ϕ . Another pleasant feature of the equation is that one does not have to add terms to it to allow for the different ionization energies W_s and W_p of the $2s$ and the $2p$ electrons of carbon, as these too do not give any dependence on ϕ . This follows because the secular determinant for the ethylene molecule factorizes, and that part which contains ϕ does not contain W_s but only W_p . Moreover, the L - S coupling of the C electrons does not give a contribution to V as the $2p\pi$ electron on each carbon nucleus has its axis of symmetry perpendicular to the plane of the other three bonds for all values of ϕ .

The energy levels of a vibrating system in the field of potential (1) can be found quite simply by quantum mechanics; in fact, Koenig⁽³⁾ has considered a much more general case, where the potential field has ν maxima and minima in the range $0 < \phi < 2\pi$. The ethylene molecule is clearly a special case with ν equal to 2. When once we know the moment of inertia of the molecule about the C-C axis, we can apply the results of Koenig's paper to find the energy levels in terms of the constant J of equation (1). Now the fundamental twisting-frequency is known from experimental data, and it is not a difficult matter to find what value of J gives agreement with the experimental figure. The energy needed to twist the planes of the CH_2 groups perpendicular to each other is simply $\frac{3}{2}J$. Since there is only one parameter in the expression for the potential energy, it is reasonable to suppose that the process we have described for determining J will give a unique result, and we find that this is the case.

Consider now that the molecule is in one of these twisting states. Classically, of course, there is zero probability of one CH_2 group swinging through an angle π and commencing to oscillate about the new equilibrium position. If the kinetic energy at $\phi = 0$ is greater than $\frac{3}{2}J$, then the angular velocity varies in magnitude but never in sign. In the quantum mechanics, however, there is a finite probability that the molecule will change from oscillating about one equilibrium position to oscillating about the other, by penetrating the potential hill. As a consequence of this resonance the twisting-levels show a doubling. We have estimated the magnitude of this doubling and find that it is of the wrong order of magnitude to be observed.

* If ϕ is increased until it reaches the vicinity of $\pi/2$, the coupling of the $2p\pi$ (double bond) electrons to zero spin is broken down, and instead they are coupled to unit spin. Allowing for this, the difference of energy of plane and perpendicular ethylene is given by $\frac{1}{2}(3C + C')$ instead of $\frac{3}{2}(C - C')$ given by equation (1). This latter therefore over-estimates the difference by $-2C'$, which is about 0.2 e.V.

§ 2. THE MATHEMATICAL CALCULATIONS

The wave equation to determine the twisting-levels is given by⁽⁴⁾

$$\frac{d^2\psi}{d\phi^2} + \frac{4\pi^2 I}{h^2} [W - V(\phi)]\psi = 0 \quad \dots\dots(2),$$

where $V(\phi)$ is given by equation (1), and I is the moment of inertia of one CH_2 group about the C-C axis. If we denote the HCH angle by $(\pi - 2\omega)$, the C-H distance by d and the mass of the hydrogen nucleus by M , then we have

$$I = 2Md^2 \cos^2 \omega = 3.31 \times 10^{-40} \quad \dots\dots(3),$$

assuming for ω the calculated value 25° and for d the C-H distance in methane, 1.10×10^{-8} cm.

As an approximation to the solution of equation (2) we assume that there is considerable resistance to twisting, so that the amplitude of ϕ is small. It is therefore permissible to expand $\cos 2\phi$ in an ascending power series in ϕ , retaining at first only terms in ϕ^2 . We have then the problem of the harmonic oscillator, and direct calculation with the value of I given in equation (3) shows that in order to fit the experimental value 750 cm^{-1} for the fundamental twisting-frequency⁽⁵⁾, we must assume that

$$J = 0.694 \text{ e.V.}$$

Since J comes out so much bigger than the fundamental itself we have justified our expansion in ϕ , and at the same time have obtained an approximate solution of equation (2). It should be explained that it was by no means obvious without examination that there was not another value for J which would give the same fundamental. A very shallow trough, for example, might have had only two vibrational levels, differing by just the fundamental. This is the possibility which our work eliminates, and we show in fact that the harmonic-oscillator approximation is quite a good one.

In order to obtain more accurate values for J and W we use the process developed by Koenig. The expansion in ϕ is made, and the effect of the various terms is calculated by straightforward perturbation theory. This method is delightfully simple and the convergence for the lowest energy levels is rapid. For those levels approaching the rotator the convergence is not so good, and one would probably have to use the implicit method described by Koenig. However, we are not interested in these levels and therefore do not worry about them. Modifying Koenig's perturbation calculations to suit our example, we find that the energy W_n of the n th twisting-state in ethylene is given by

$$W_n = \frac{h}{\pi} \left[\frac{3J}{2I} \right]^{\frac{1}{2}} \left[(n + \frac{1}{2}) - (2n^2 + n + 1)/16k - (2n^3 + 3n^2 + 3n + 1)/128k^2 \dots \right] \quad \dots\dots(4),$$

where $kh = \pi \left[\frac{3}{2} JI \right]^{\frac{1}{2}}$. Using our value $J = 0.694$, we obtain $k = 11.3$. Substituting back in equation (4) we find that it is necessary to adjust J to 0.718 e.V. in order to preserve the fundamental twisting-frequency at 750 cm^{-1}

To illustrate the points we have just explained, we give in the table the energy levels of the harmonic oscillator W_h with our final value for J of 0.718 e.V., and with them the accurate values of W_a calculated from the field of potential (1). It will be noticed that the higher levels deviate considerably from the harmonic-oscillator approximation; in other words, there is a considerable convergence factor. Since any twisting-frequency is inactive, the twisting-levels have to be obtained experimentally from combination bands, and with these the intensity falls off rapidly with the order. There is little hope at the moment, therefore, of comparing our convergence factor with the experimental value.

n	0	1	2	3	4
W_h	381	1144	1907	2670	3433
W_a	377	1127	1859	2572	3265

§ 3. COMPARISON WITH PREVIOUS WORK

We have seen that in order to get the right value for the fundamental twisting-frequency in ethylene it is necessary to assume that the exchange integral J has the value 0.72 e.V. This gives about 1 e.V. for the energy required to twist one CH_2 group perpendicular to the other, an estimate which should be accurate to within 20 per cent. The value given by Pauling and Wheland⁽⁶⁾ for the exchange integral J in benzene is $1.50 + 0.10$ e.V., obtained from thermo-chemical data. Values were assigned to various chemical bonds and were adjusted to give the correct free energies of various compounds in which there is no possibility of resonance between different structures. Using these values for structures in which there is resonance, the difference between the estimated and observed free energies must be due to the resonance itself. The calculated effect of the resonance is simply a numerical multiple of J , and thus J is determined. The present author is a little sceptical of the accuracy which is claimed for this method. One would not expect the integral J to be exactly the same in ethylene as it is in benzene, but the two should differ by only a few per cent. The difference between our estimate and Pauling and Wheland's is too large to be accounted for in this way.

The only attempt at a numerical calculation of J is that of Bartlett⁽⁷⁾, and there is a little difficulty in reconciling his figures with ours. It is not possible to get agreement between the values of Bartlett and those of Pauling and Wheland. If one assumes that the effective nuclear charge of the carbon atom towards the $2p\pi$ electron of the double bond is 2.5 and that the internuclear distance is 1.2 Å., Bartlett's value for J is 0.74 e.V. This agrees well with our figure but has been obtained only by assuming a rather large effective nuclear charge.

There is one other way of obtaining a check on the value of J , and that is from the observed heat of activation of compounds derived from ethylene. If one of the H atoms in each CH_2 group is replaced by a (COOCH_3) group, there are two possible forms for the resulting molecule, and it is possible to distinguish between

them because they have different chemical properties. The kinetics of the reaction has been studied by Nelles and Kistiakowsky⁽⁸⁾, who found that the heat of activation of one form to the other is 26.5 kcal./mol. (1.15 e.V.). They concluded from chemical evidence that the activation energy represents almost exclusively the straining of the double bond on a 90° rotation of one relative to the other of the two atomic groups of the molecule. Although the bonds in this example are not quite the same as those in ethylene, one would expect the dependence of the energy W on ϕ to be very similar in the two cases. This is borne out by the good agreement between the above value 1.15 e.V. of Nelles and Kistiakowsky and our value 1.0 ± 0.2 e.V., obtained from the fundamental twisting-frequency.

In conclusion, we consider the possible error which exists in our estimate of J . First of all there is some uncertainty in the exact value for the fundamental, but this should not be more than a few wave-numbers, unless indeed the 750 cm^{-1} is not a twisting-frequency at all. This possibility seems to be ruled out fairly conclusively by the observed character of the infra-red absorption bands. A much more likely source of error is in the value we have used for the moment of inertia about the C-C axis. The C-H distances and the angle ω are not known very accurately and there may easily be an error of 5 per cent in I . This gives a possible error of about 10 per cent in J .

§ 4. ACKNOWLEDGMENT

The author wishes to thank Drs Sutherland and Melville for helpful discussion.

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ANOMALOUS CHANGES IN TEMPERATURE DUE TO THERMIONIC EMISSION IN THE FILAMENTS OF VALVES

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ABSTRACT. A triode valve should show, for a given filament current, a steady filament-temperature, lower when the anode is at a positive than when it is at a negative or zero potential. It has been found that in some valves the steady filament-temperature is lower when the anode is positive, as would be expected, but in other valves it is higher. It is shown that this anomalous increase in temperature is due to radiation from the anode and is larger for valves having a high anode dissipation and an anode which closely surrounds the filament. It is shown that when a correction for this effect has been applied the work function can be approximately calculated from measurements made on an ordinary valve.

RICHARDSON'S equation for the thermionic saturation current is $i = aT^{\frac{1}{2}}e^{-\phi/kT}$, a being a constant, T the absolute temperature, ϕ the thermionic work function, supposed independent of T , and k Boltzmann's constant. The average energy of thermal agitation of the electrons is $2kT$ so that they carry away per second a total of u ergs, where

$$u = \frac{i}{e}(\phi + 2kT),$$

e coulombs being the electronic charge.

On writing $\phi = Ve$ we have

$$u = i \left(V + \frac{2k}{e} T \right) = iw,$$

where w is the loss of energy per ampere per second due to the thermionic emission.

Any valve filament will thus be cooled by the emission of electricity, and there will be a change in its resistance. From the measured change in resistance one can find the change in temperature.

Experiments on this effect have been made by various workers^(1,...8). The results obtained in the present investigation are apparently partially opposed to those obtained by several previous observers, especially Lester⁽⁴⁾ and Davisson and Germer^(6,7). It must be particularly noted, however, that these observers worked with carefully designed *diodes* constructed specially for investigation purposes. The observations made were clearly of an accurate nature, but the difference in the present case is that ordinary well-known commercial makes of *triode* have been

submitted to test. Certain aspects of anomalous behaviour in such commercial triodes are what the present paper records.

Tieri and Ricca⁽⁹⁾ pointed out in 1928 that the emission entails a variation in the effective heating-current, and that this provides a means of finding the intrinsic potential of some metals. They also were working with triodes.

On change of the anode potential from a large negative to a positive value there will be a decrease in filament temperature due wholly to the emission, provided that the temperature of the surroundings does not change and that the supply of heat is unaltered. The electron current decreases the effective heating-current so that there will be a drop in temperature due to this cause. But unless the anode is specially cooled the filament will be in an enclosure of increasing average temperature. The extra heat received from the enclosure will diminish the cooling, and when equilibrium is reached may be enough to mask it completely. Whether or not this will happen depends on the shape of the anode and its rise in temperature.

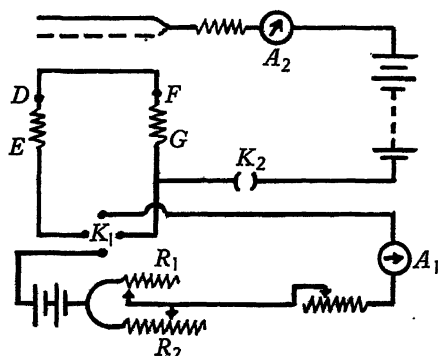


Figure 1.

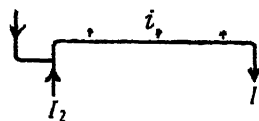


Figure 2.

The experimental arrangements are indicated in figure 1. A_1 and A_2 are ammeters showing respectively the approximate magnitudes of the heating and anode currents. The rheostats R_1 and R_2 in parallel regulate the filament current. DE and FG are two 1-ohm standard resistance coils, of which the potential terminals can be connected to a potentiometer through a suitable commutator. The keys K_1 and K_2 serve to open or reverse the battery connexions to the filament and anode. The potential-differences V_1 and V_2 between the terminals of the resistance coils and V_3 between the filament pins were measured in the usual way with a potentiometer. Accumulators were used as sources of potential. In all cases the grid and anode were directly connected.

On reference to figure 2 it is clear that I_1 and I_2 , the currents in the negative and positive leads to the filament, are unequal, the difference $(I_1 - I_2)$ or i being the thermionic current. As i is measured directly by the milliammeter A_2 a leak would be shown at once by a discrepancy between the readings. Assuming the emission to be constant along the length of the filament the effective heating-current will be very nearly $\frac{1}{2}(I_1 + I_2)$, the mean of the values at the ends.

The potential-difference V_s between the filament terminals being measured, we have for the resistance R of the filament

$$R = \frac{2V_s}{I_1 + I_2} - s.$$

The pins, supports, and leads for the filaments in the valves used in this work are not surrounded by the anode; consequently their resistance will not vary much with its temperature. s , which is the resistance of these conductors, will therefore be nearly constant, and being small may be neglected.

If curves be drawn with the filament-resistances as ordinates and heating-currents as abscissae, for the cases where the anode is (a) negative and (b) positive, their general form will be that shown in figures 4 and 5. It appears that the filament-temperature is decreased by the emission; but in some cases, as in valves like Mullard P.M. 252 for example, the curves have the general shape of those in figure 3, indicating an increase of temperature when the anode is positive. The

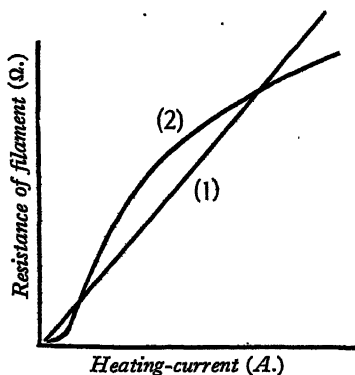


Figure 3. (1) H.t. off; (2) h.t. on.

resistance of the filament varies with the time during which the anode current has been flowing, and so does the increase in temperature in these cases. Four valves of this type gave nearly the same results. Other valves such as Osram L.S. 5 which have a larger anode surface per watt dissipated, and ones like R. 5 V. with a smaller total anode dissipation, do not show this heating.

That this reversal of the usual effect is due to heat received from the anode is made clear if the course of an experiment is so ordered that the anode remains at a nearly constant temperature. This may be done by closing the anode circuit and immediately thereafter the galvanometer circuit of the potentiometer connected across the filament pins; if balance is not obtained both circuits are opened, an interval is allowed for cooling, and the potentiometer is readjusted. The process is continued until balance is obtained. Alternatively the anode circuit may be kept normally closed and measurements made when it is momentarily opened. The observations recorded were made by the first method.

A Mullard P.M. 252 valve was examined in this way; the curves have the form shown in figures 4 and 5. There is now no range over which heating takes place.

From the curves showing the relations between i and R , figures 4 and 5, we can calculate approximately the work function ϕ for the material of the filament. Suppose that a line parallel to the I axis is drawn to cut the curves. The points of intersection have for abscissae I' and I'' , the values of the heating-current required to bring the filament to the same resistance in the two cases. From the curve

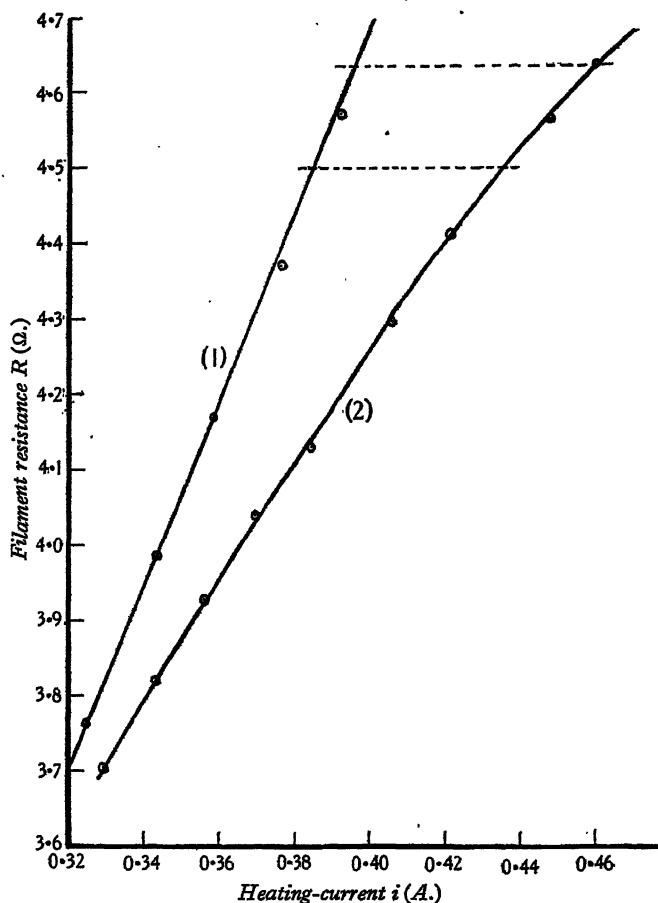


Figure 4. Mullard P.M. 252. H.t. to negative end of filament. (1) H.t. off; (2) h.t. on.

showing the relation between I and i , figure 6, we find the thermionic emission. Since the filament has the same temperature in both cases the losses by conduction, radiation, etc. are equal, and the energy u carried away by the electrons is given by

$$u = (I'^2 - I''^2) R,$$

while $w = u/i$. Since the number of electrons leaving per second is $i/1.5 \times 10^{-18}$ the loss L in ergs per electron is given by

$$L = 1.5 \times 10^{-18} w \text{ ergs.}$$

A summary of results on four kinds of valve is shown in the table.

Table

Type of valve	i (mA.)	L (ergs $\times 10^{-13}$)	End of filament to which h.t. is connected
P.M. 252	124.5	3.28	+
	95.7	3.04	
	120.6	3.38	
	95.7	3.03	
L.S. 5	125.0	7.25	+
	107.2	6.76	
	120.3	6.70	
	137.2	6.85	
R. 5 V. (an old specimen)	74.1	10.72	+
	57.0	10.01	
	81.6	10.20	
	62.0	9.90	
V.T. 10	77.4	7.55	+
	62.7	7.32	
	84.1	6.69	
	65.7	6.61	

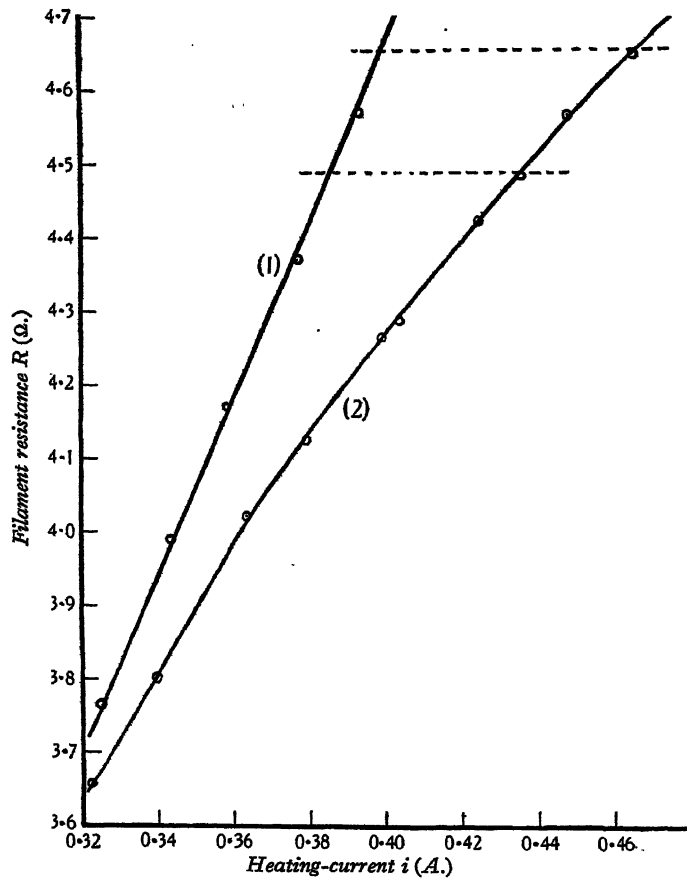


Figure 5. Mullard P.M. 252. H.t. to positive end of filament. (1) H.t. off; (2) h.

To sum up we may say that: (1) In an ordinary small valve, the cooling of the filament due to its thermionic emission may be masked by radiation from the anode. (2) Whether the effect takes place or not depends on the construction of the valve and on the working-temperature of the anode. Power valves may show a considerable rise in temperature. (3) The work function can be calculated where suitable corrections are made, though with considerable error.

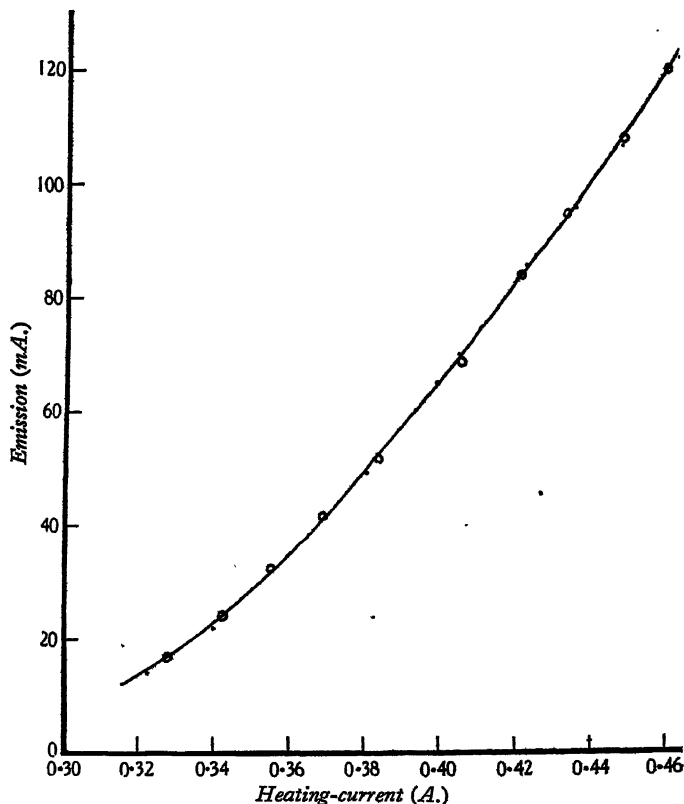


Figure 6. Mullard P.M. 252. • H.t. to positive end of filament.
○ H.t. to negative end of filament.

In conclusion I should like to express my thanks to Prof. T. L. Rosgyll Ayres for his encouragement and for placing the resources of the laboratory at my disposal.

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CHANGE OF VARIABLES IN LAPLACE'S AND OTHER SECOND-ORDER DIFFERENTIAL EQUATIONS

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ABSTRACT. Transformations of variables are expressed as matrix products, the effect of transposition being particularly considered, and the results applied to the transformation of the general second-order differential expression.

CHANGES in the independent variables in Laplace's and other equations occurring in mathematical physics are usually considered separately for each equation, and are often carried out in a somewhat clumsy fashion. A convenient general form in which to express the result of changing from a set of variables $\alpha, \beta, \gamma, \delta, \dots$ to an equivalent set a, b, c, d, \dots is obtainable if the equation is expressed as a matrix product. Let J denote the Jacobian $\frac{\partial(a, b, c, d, \dots)}{\partial(\alpha, \beta, \gamma, \delta, \dots)}$, j the corresponding matrix

$$\begin{pmatrix} a_{\alpha} & a_{\beta} & a_{\gamma} & \dots \\ b_{\alpha} & b_{\beta} & b_{\gamma} & \dots \\ c_{\alpha} & c_{\beta} & c_{\gamma} & \dots \\ \dots & \dots & \dots & \dots \end{pmatrix}.$$

(where suffixes indicate differentiation), and j' the matrix conjugate to j formed by turning the first, second ... horizontal row into the first, second ... vertical column or *vice versa*. Also let Δ and D respectively denote the operators

$$\left(\frac{\partial}{\partial \alpha} \quad \frac{\partial}{\partial \beta} \quad \frac{\partial}{\partial \gamma} \dots \right) \quad \text{and} \quad \left(\frac{\partial}{\partial a} \quad \frac{\partial}{\partial b} \quad \frac{\partial}{\partial c} \dots \right)$$

regarded as linear matrices, and Δ' and D' the corresponding transposed vertical operators. Then if ϕ is the dependent variable, ψ a given function of $\alpha, \beta, \gamma, \dots$ and Θ a square matrix, of order not exceeding the number of independent variables, whose elements are either constants or functions of $\alpha, \beta, \gamma, \dots$, the equation

$$\Delta \Theta \Delta' \phi = \psi$$

becomes on change of variables

$$J D J^{-1} j \Theta j' D' \phi = \psi,$$

where, in accordance with the usual convention, the differential operators act on all factors written on their right. This formula is interesting as showing that the simplification of all equations of this type depends upon finding a j which reduces $j \Theta j'$ to a canonical form.

For readers who are not accustomed to the use of matrices it may be helpful to illustrate by an example the connexion between an expression $\Delta\Theta\Delta'\phi$ and the ordinary form. Let us suppose there are three independent variables α, β, γ , and that Θ denotes the matrix

$$\begin{pmatrix} l & m & n \\ p & q & t \\ u & v & w \end{pmatrix},$$

where the elements $l, m, \dots w$ may be either constants or functions of α, β, γ . Then, in accordance with the fundamental matrix convention that in multiplication a horizontal row of a left-hand factor is associated term by term with a vertical row of a right-hand factor, $\Delta\Theta\Delta'\phi$ denotes

$$\frac{\partial}{\partial \alpha} \left(l \frac{\partial \phi}{\partial \alpha} + m \frac{\partial \phi}{\partial \beta} + n \frac{\partial \phi}{\partial \gamma} \right) + \frac{\partial}{\partial \beta} \left(p \frac{\partial \phi}{\partial \alpha} + q \frac{\partial \phi}{\partial \beta} + t \frac{\partial \phi}{\partial \gamma} \right) + \frac{\partial}{\partial \gamma} \left(u \frac{\partial \phi}{\partial \alpha} + v \frac{\partial \phi}{\partial \beta} + w \frac{\partial \phi}{\partial \gamma} \right).$$

It often happens that a relation expressed by a differential equation involves the differential coefficients in a way which naturally finds its expression in a form of this kind. The matrix Θ can then be written down immediately. One of the merits of the transformation formula to be established is that when the variables are changed the new equation is obtained directly in this convenient form.

When the coefficients in the equation are constants the matrix can always be written down immediately. Thus the equation

$$\frac{\partial^2 U}{\partial x^2} + \frac{\partial^2 U}{\partial y^2} + \lambda \left(\frac{\partial^2 U}{\partial x \partial z} + \frac{\partial^2 U}{\partial y \partial z} \right) = V$$

is formally the same as

$$\begin{pmatrix} \frac{\partial}{\partial x} & \frac{\partial}{\partial y} & \frac{\partial}{\partial z} \end{pmatrix} \Theta \begin{pmatrix} \frac{\partial}{\partial x} \\ \frac{\partial}{\partial y} \\ \frac{\partial}{\partial z} \end{pmatrix} U = V,$$

where

$$\Theta = \begin{pmatrix} 1 & 0 & \lambda \\ 0 & 1 & \lambda \\ 0 & 0 & 0 \end{pmatrix}$$

provided λ is a constant or a function of z only. If λ is a constant we may write Θ in other forms, for example the symmetrical form

$$\begin{pmatrix} 1 & 0 & \frac{1}{2}\lambda \\ 0 & 1 & \frac{1}{2}\lambda \\ \frac{1}{2}\lambda & \frac{1}{2}\lambda & 0 \end{pmatrix}$$

by making use of the relations

$$\frac{\partial^2 U}{\partial x \partial z} = \frac{\partial^2 U}{\partial z \partial x}, \quad \frac{\partial^2 U}{\partial y \partial z} = \frac{\partial^2 U}{\partial z \partial y}.$$

When the elements of Θ are not constants we shall usually have first order differential

coefficients of the dependent variable in the equation, and there may also be a term involving the dependent variable undifferentiated. We may bring all these terms into the standard form we have assumed by introducing a dummy unit variable. For example if the coefficients a, b, c, \dots are arbitrary functions of x and y , the expression

$$av_{xx} + 2hv_{xy} + bv_{yy} + 2gv_x + 2fv_y + cv$$

may be written

$$\begin{pmatrix} \frac{\partial}{\partial x} & \frac{\partial}{\partial y} & \frac{\partial}{\partial z} \end{pmatrix} \begin{pmatrix} a & h & g' \\ h & b & f' \\ g' & f' & c' \end{pmatrix} \begin{pmatrix} \frac{\partial}{\partial x} \\ \frac{\partial}{\partial y} \\ \frac{\partial}{\partial z} \end{pmatrix} vx^2,$$

where after differentiation z is replaced by unity, and

$$4f' = 2f - h_x - b_y$$

$$4g' = 2g - a_x - h_y$$

$$4c' = 2c - 2g_x - 2f_y + a_{xx} + 2h_{xy} + b_{yy}.$$

When there are n independent variables the total number of coefficients in the linear second order expression is $\frac{1}{2}(n+1)(n+2)$ and this is exactly the number of independent elements in the symmetrical square matrix of order $n+1$. It follows that this matrix form for the equation is always possible. By the use of an unsymmetrical matrix a dummy variable can often be avoided without difficulty. Alternatively we may use the transformation formula to be obtained for the second order terms only, and deal with the remaining terms by the simple first order relations.

The most familiar of all transformations to the physicist is perhaps that from rectangular cartesian to polar coordinates. The fundamental equations are

$$x = r \sin \theta \cos \phi, \quad y = r \sin \theta \sin \phi, \quad z = r \cos \theta.$$

The values of j and J may be derived from these indirectly by making use of the fact that j is the inverse of the matrix i employed later. A direct determination follows from the equivalent equations

$$r = (x^2 + y^2 + z^2)^{\frac{1}{2}}, \quad \theta = \tan^{-1} \{ (x^2 + y^2)^{\frac{1}{2}} z^{-1} \}, \quad \phi = \tan^{-1} (yx^{-1}).$$

The expressions reached are

$$j = \begin{pmatrix} \sin \theta \cos \phi & \sin \theta \sin \phi & \cos \theta \\ r^{-1} \cos \theta \cos \phi & r^{-1} \cos \theta \sin \phi & -r^{-1} \sin \theta \\ -r^{-1} \operatorname{cosec} \theta \sin \phi & r^{-1} \operatorname{cosec} \theta \cos \phi & 0 \end{pmatrix}$$

and

$$J^{-1} = r^2 \sin \theta.$$

If this transformation is to be applied to the equation which, written in full, is

$$\frac{\partial}{\partial x} \left(l \frac{\partial \kappa}{\partial x} + m \frac{\partial \kappa}{\partial y} + n \frac{\partial \kappa}{\partial z} \right) + \frac{\partial}{\partial y} \left(p \frac{\partial \kappa}{\partial x} + q \frac{\partial \kappa}{\partial y} + t \frac{\partial \kappa}{\partial z} \right) + \frac{\partial}{\partial z} \left(u \frac{\partial \kappa}{\partial x} + v \frac{\partial \kappa}{\partial y} + w \frac{\partial \kappa}{\partial z} \right) = k,$$

and which, as we have already seen, corresponds to

$$\Theta = \begin{pmatrix} l & m & n \\ p & q & t \\ u & v & w \end{pmatrix},$$

the result in polar coordinates, written at length, is

$$\begin{aligned} \frac{\partial}{\partial r} \left(L \frac{\partial \kappa}{\partial r} + M \frac{\partial \kappa}{\partial \theta} + N \frac{\partial \kappa}{\partial \phi} \right) + \frac{\partial}{\partial \theta} \left(P \frac{\partial \kappa}{\partial r} + Q \frac{\partial \kappa}{\partial \theta} + T \frac{\partial \kappa}{\partial \phi} \right) \\ + \frac{\partial}{\partial \phi} \left(U \frac{\partial \kappa}{\partial r} + V \frac{\partial \kappa}{\partial \theta} + W \frac{\partial \kappa}{\partial \phi} \right) = kr^2 \sin \theta, \end{aligned}$$

where the new coefficients are given by the matrix equation

$$\begin{pmatrix} L & M & N \\ P & Q & T \\ U & V & W \end{pmatrix} = r^2 \sin \theta \cdot j \Theta j'.$$

As a simple example take

$$l = q = w = \rho, \quad -m = p = \nu,$$

$$n = -u = \mu, \quad -t = v = \lambda.$$

On multiplying together the three matrices we easily find

$$L = \rho r^2 \sin \theta, \quad Q = \rho \sin \theta, \quad W = \rho \operatorname{cosec} \theta,$$

$$M = -P = r \sin \theta (\lambda \sin \phi - \mu \cos \phi),$$

$$N = -U = r (\lambda \cos \theta \cos \phi + \mu \cos \theta \sin \phi - \nu \sin \theta),$$

$$V = -T = \lambda \sin \theta \cos \phi + \mu \sin \theta \sin \phi + \nu \cos \theta.$$

We may now turn to the theorem itself. The only feature of the proof which is not quite direct is that which results in the introduction of the factors J and J^{-1} on inverting the order of some of the matrices. It does not involve any actual difficulty in a direct proof, but we shall make use here of a theorem of Jacobi's. This states that if A, B, C, \dots are the cofactors of the elements in order of any row of the Jacobian

$$\begin{vmatrix} \alpha_a & \alpha_b & \alpha_c & \dots \\ \beta_a & \beta_b & \beta_c & \dots \\ \gamma_a & \gamma_b & \gamma_c & \dots \\ \dots & \dots & \dots & \dots \end{vmatrix},$$

then

$$\frac{\partial A}{\partial a} + \frac{\partial B}{\partial b} + \frac{\partial C}{\partial c} + \dots = 0.$$

The sum on the left clearly involves only products of first differential coefficients with one second differential factor in each term. Taking the top row for illustration, the factors involving double differentiation with respect to a and b can only arise

from the first two terms, and their sum is obviously

$$\begin{vmatrix} 1 & . & . & . & \dots \\ . & \beta_{ab} & \beta_c & \beta_d & \dots \\ . & \gamma_{ab} & \gamma_c & \gamma_d & \dots \\ . & \delta_{ab} & \delta_c & \delta_d & \dots \\ \dots & \dots & \dots & \dots & \dots \end{vmatrix} + \begin{vmatrix} . & 1 & . & . & \dots \\ \beta_{ab} & . & \beta_c & \beta_d & \dots \\ \gamma_{ab} & . & \gamma_c & \gamma_d & \dots \\ \delta_{ab} & . & \delta_c & \delta_d & \dots \\ \dots & \dots & \dots & \dots & \dots \end{vmatrix}$$

which vanishes. Similarly all the other terms vanish.

Now let i denote the matrix

$$\begin{pmatrix} \alpha_a & \alpha_b & \alpha_c & \dots \\ \beta_a & \beta_b & \beta_c & \dots \\ \gamma_a & \gamma_b & \gamma_c & \dots \\ \dots & \dots & \dots & \dots \end{pmatrix},$$

i' the transposed matrix, and I the corresponding determinant. Then, using also Δ , Δ' , D , D' , j , j' and J in the sense explained in enunciating the theorem, the ordinary equations of transformation for differential coefficients are

$$\Delta' = j' D' \text{ and } D' = i' \Delta'.$$

These involve $ij = ji = 1$, and $IJ = 1$. If we wished to transpose these equations as they stand we should have to adopt some such form as

$$\Delta = D j_0, \quad D = \Delta i_0,$$

where the zero suffixes indicate that the expressions to which they are attached are not to be subject to the operators which immediately precede them. Such restriction is most inconvenient, and we proceed to remove it.

Let $A_\pi, B_\pi, C_\pi \dots$ be the cofactors of the row $\pi_a, \pi_b, \pi_c \dots$ of I . Then by Jacobi's theorem, whatever ϕ may be

$$\frac{\partial A_\pi \phi}{\partial a} + \frac{\partial B_\pi \phi}{\partial b} + \frac{\partial C_\pi \phi}{\partial c} + \dots = A_\pi \frac{\partial \phi}{\partial a} + B_\pi \frac{\partial \phi}{\partial b} + C_\pi \frac{\partial \phi}{\partial c} + \dots$$

But since $ij = 1$

$$A_\pi = I a_\pi, \quad B_\pi = I b_\pi,$$

and so on, and the equation above is therefore the same as

$$\begin{aligned} DI \begin{pmatrix} a_\pi \\ b_\pi \\ c_\pi \\ \dots \end{pmatrix} \phi &= (A_\pi \ B_\pi \ C_\pi \ \dots) D' \phi \\ &= (A_\pi \ B_\pi \ C_\pi \ \dots) i' \Delta' \phi \\ &= I \frac{\partial \phi}{\partial \pi} \end{aligned}$$

by a fundamental property of the elements of a determinant and their cofactors. Putting $\alpha, \beta, \gamma, \dots$ in turn for π we have

$$DI j \phi = I \Delta \phi,$$

or since $IJ = 1$

$$\Delta \phi = J D J^{-1} j \phi.$$

As ϕ is arbitrary we may replace it by $\Theta \Delta' \phi$, which, as we have already seen, is equal to $\Theta j' D' \phi$; the general second order transformation formula

$$\Delta \Theta \Delta' \phi = J D J^{-1} j \Theta j' D' \phi$$

then follows.

To illustrate the application of this formula take $\Theta = 1$; on the left $\Delta \Delta' \phi$ represents the general Laplacian expression. Its form will be unaltered on changing the variables if, and only if, $j j' = 1$, i.e. if j is an orthogonal matrix, or if $a = \text{const.}$, $b = \text{const.}$, etc., intersect mutually at right angles. More generally by substituting any scalar function f for Θ we see that the same conclusion holds for the equation

$$\frac{\partial}{\partial \alpha} \left(f \frac{\partial \phi}{\partial \alpha} \right) + \frac{\partial}{\partial \beta} \left(f \frac{\partial \phi}{\partial \beta} \right) + \frac{\partial}{\partial \gamma} \left(f \frac{\partial \phi}{\partial \gamma} \right) + \dots = \psi.$$

AN INSTRUMENT FOR ELECTRICAL PROSPECTING BY THE INDUCTIVE METHOD

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ABSTRACT. This paper deals with an examination of the conditions in the Bieler-Watson method of geophysical surveying, and demonstrates that, in general, the horizontal field is not in quadrature with the vertical field. An instrument has been designed which will allow the horizontal field to be compared completely with the vertical field, the important feature of the instrument being that the horizontal components in phase and in quadrature with the vertical field are obtained directly from the instrument readings. The apparatus has been tested on elliptically polarized fields and has given satisfactory results.

§ 1. INTRODUCTION

THE work described is the outcome of an attempt to improve the usefulness of the Bieler-Watson method of electrical prospecting, by modifying it in such a way that the associated magnetic fields may be measured more precisely and without neglecting components which in fact exist. The Bieler-Watson method was used with some success during the Imperial Geophysical Experimental Survey in Australia in 1928-30, but experiences in the field showed in what respects it was lacking.

§ 2. THE INDUCTIVE METHODS OF PROSPECTING

In the inductive method of geophysical prospecting, an alternating magnetic field is applied to the ground under examination, by means of a large loop of wire conveying alternating current and laid on the ground-surface. The magnetic field induces eddy currents in the neighbouring rocks and consequently the resultant magnetic field at any point is made up of two parts, the primary applied field and the secondary field due to the eddy currents. In general the resistivities of the rocks are large, so that the eddy currents and the secondary field are small. If, however, a good conductor, such as a sulphide-ore body, is in the vicinity, the secondary field may attain values of the same order as the primary field. By making measurements of the magnetic field at the earth's surface the position of the good conductor may be inferred from the large values of the secondary field.

If it is assumed that the surrounding rocks are non-conductors the secondary field will be due to the good conductor only. The e.m.f. producing the currents is proportional to the rate of change of magnetic flux through the body, and will differ in phase by 90° from the primary magnetic field. Further, if the eddy-current paths have negligible reactance the currents themselves, and hence the secondary

field, will be in quadrature with the primary field. Since the two fields have different directions the resultant field to be measured is elliptically polarized. At points on the ground-surface the primary field is vertical and, if the measurements are made within the loop at a sufficient distance from the cable, it is constant in amplitude to 2 per cent over a large area. If the vertical component of the secondary field is small compared with the primary field, the vertical field in the loop may be regarded as a magnetic field of standard amplitude and phase. The horizontal component of the secondary field is measured in terms of the vertical field, and with the assumptions made these two fields are in quadrature.

The Bieler-Watson* apparatus used for this determination consists of two coils at right angles so that there is no mutual interaction between them, one coil being placed in a vertical plane and the other in a horizontal plane. The e.m.f.s induced

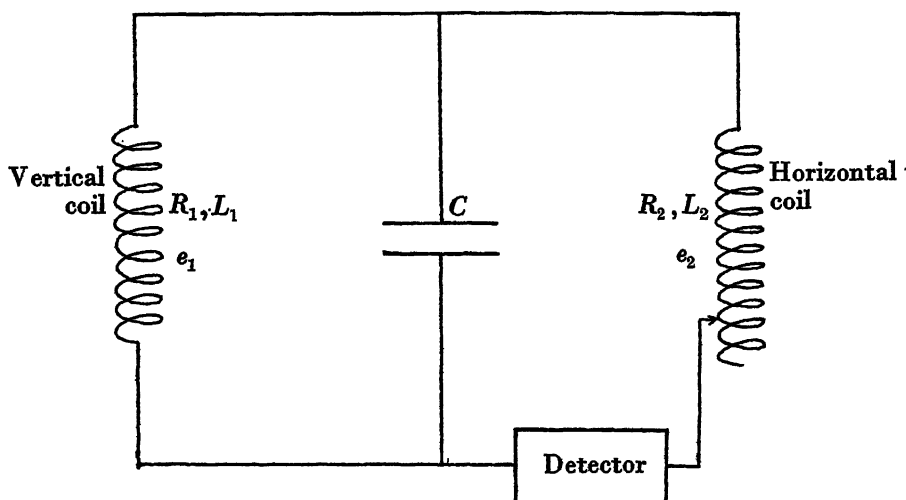


Figure 1.

in the coils by the magnetic fields are in quadrature, but if the vertical coil is tuned with a condenser the e.m.f. across the condenser will be in phase with the e.m.f. in the horizontal coil, and by varying the number of turns in the latter the system can be balanced, figure 1. Let H and V be the amplitudes of the horizontal and vertical fields, and e_1 and e_2 the amplitudes of the corresponding e.m.f.s in the two coils. Then

$$e_1/e_2 = A_V N_V \cdot H / A_H N_H \cdot V,$$

where A_V , A_H are the effective areas of each turn and N_V , N_H the numbers of turns of the vertical and horizontal coils respectively. With the notation of figure 1 the balance condition for the circuit is given by

$$e_1/e_2 = -j\omega C R_1$$

or

$$H/V = -j\omega C R_1 \cdot A_H N_H / A_V N_V = -jk N_H \dots\dots(1),$$

* Broughton, Edge and Laby, *Principles and Practice of Geophysical Prospecting* (Camb. Univ. Press, 1931).

where k is a constant of the instrument. Hence the number of turns of the horizontal coil required for balance is a measure of the ratio V/H . Thus by measuring N_H at various parts of the field the variation of the horizontal component of the secondary field may be obtained and the position of the good conductor inferred. Equation (1) can only be satisfied if H and V differ in phase by 90° , and for any other phase relation balance cannot be obtained. In practice it is found that minima only are obtained, and in many cases the minima are so broad that the readings are useless. The occurrence of minima rather than true balance points has been attributed to harmonics, in spite of the fact that tuned amplifiers were used as detectors. Efforts were made to improve the sharpness of balance by rocking the system about a horizontal axis, in which case the greatest intensity-variation will be obtained on balance if the residual note is due to harmonics. This method is open to suspicion, as the balance condition may not correspond to the vertical position of the tuned coil.

There are many reasons, both practical and theoretical, why the simple assumption concerning the quadrature relation between the fluxes threading the two coils is not justified. A small tilt of the tuned coil, or a deviation of the primary field from the vertical due to local topography, will produce an in-phase e.m.f. in the vertical coil. At the same time the vertical component of the secondary field will produce a quadrature component in the horizontal coil. On theoretical grounds it is to be expected that the primary magnetic field will be appreciably absorbed as it passes down through the country rock to the good conductor, and in general this is accompanied by a phase-change. Hence the flux through the ore body is no longer in phase with the primary field, and for the same reason the secondary field at the surface is not in phase with the eddy currents producing it. The skin effect in the ore bodies is usually pronounced on account of their dimensions and low resistivity; consequently the phase of the eddy currents will vary from point to point, again influencing the phase of the secondary field. In many cases the magnetic field due to a current passed conductively through the ground is examined, and here the resultant field is even more complicated in structure.

It is apparent that a more suitable instrument is necessary for this type of prospecting, which will allow the phase as well as the amplitude of the horizontal component to be determined. The object of the present investigation is to examine methods which would allow this to be accomplished and, if possible, to design a direct-reading instrument which would allow the in-phase and quadrature components of the horizontal field to be measured in terms of the vertical field without further calculation.

§ 3. CIRCUITS INVOLVING PHASE-MEASUREMENTS

By introducing a small resistance in the condenser arm of the original double coil circuit, small variations of the horizontal field from quadrature may be taken into account. With the notation of figure 2

$$\left. \begin{aligned} (R_1 + r + L_1 j\omega - j/\omega C) \cdot u - (s - j/\omega C) \cdot v - e_1 &= 0 \\ - (s - j/\omega C) \cdot u + (R_2 + s + G + L_2 j\omega - j/\omega C) \cdot v - e_2 &= 0 \end{aligned} \right\} \dots (2),$$

whence, if $L_1\omega = 1/\omega C$, the balance condition becomes

$$e_1/e_2 = -(R_1 + r)/(s - j/\omega C).$$

From this equation, both the in-phase and the quadrature component of e_1 and hence of H may be determined. If the balance condition be written in the form

$$e_2 = -u(s - j/\omega C),$$

it is seen that phase angles in the quadrant 0 to $-\pi/2$ may be obtained, while, by reversing the leads to the horizontal coil, phases in the quadrant $\pi/2$ to π may

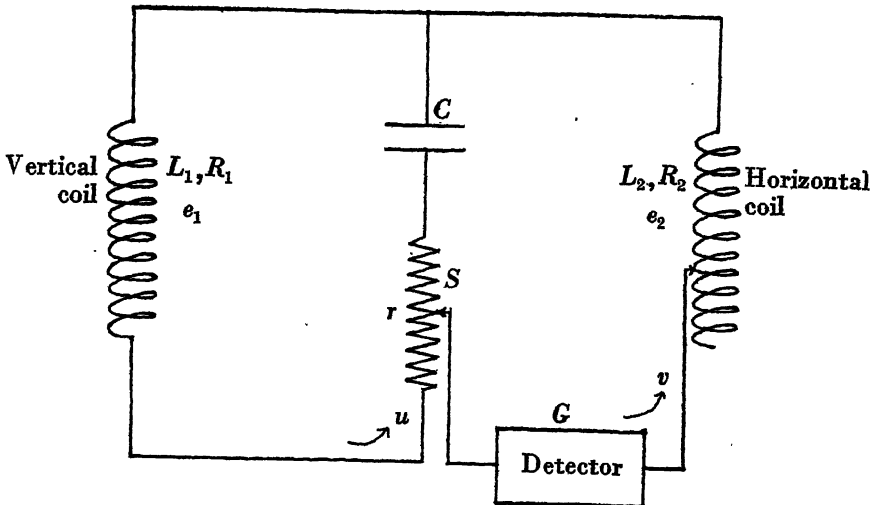


Figure 2.

be measured. For small deviations from quadrature the instrument is direct-reading, for

$$|e_1/e_2| \approx \omega C (R_1 + r)$$

and the angle of deviation δ , assumed small, is given by

$$\delta = \tan^{-1}(-\omega Cs) \propto s.$$

By replacing the condenser by a variable mutual inductance, with both search coils fixed, a system which allows any phase angle to be measured is obtained. The balance is secured by varying the mutual inductance and the tapping of the resistance, figure 3. If L_2, R_2 are the total inductance and resistance in the current AB , and L_1, R_1 the corresponding values for the vertical coil C and the secondary winding of the mutual inductance, the equations for the currents in the two nets are

$$\begin{cases} (R_2 + L_2 j\omega) \cdot u - (s + M j\omega) \cdot v - e_2 = 0 \\ -(s + M j\omega) \cdot u + (R_1 + s + L_1 j\omega) \cdot v - e_1 = 0 \end{cases} \quad \dots\dots(3)$$

and the balance condition is

$$e_1/e_2 = -(s + M j\omega)/(R_2 + L_2 j\omega)$$

or

$$e_1 = -u(s + M j\omega).$$

Since the signs of both u and M may be changed, the instrument allows all phase angles to be measured since any combination of signs in the formula

$$e_1 = \pm (s \pm Mj\omega) \cdot u$$

may be obtained. For any frequency $\omega_0/2\pi$ an instrument of the type may be made direct reading if the mutual inductance is calibrated to give $M\omega_0$ in ohms. If in equation (3) $R_2 = L_2\omega_0$ the balance condition assumes the form

$$\begin{aligned} \frac{e_1}{e_2} &= -\frac{1}{R_2} \left\{ \frac{s}{1+j} + j \frac{M\omega_0}{1+j} \right\} \\ &= -\frac{1}{2R_2} \{ (M\omega_0 + s) + j(M\omega_0 - s) \} \quad \dots\dots(4). \end{aligned}$$

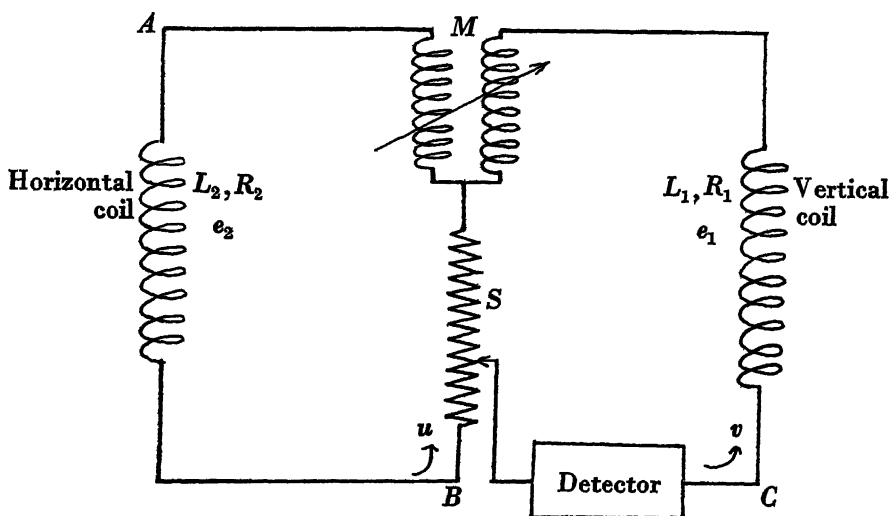


Figure 3.

Hence addition and subtraction of the readings gives the in-phase and quadrature components immediately. For any other frequency, if $R_2 = L_2\omega$,

$$\frac{e_1}{e_2} = -\frac{1}{2R_2} \left\{ \left(M\omega_0 \cdot \frac{\omega}{\omega_0} + s \right) + j \left(M\omega_0 \cdot \frac{\omega}{\omega_0} - s \right) \right\}$$

and a simple factor serves to convert both readings to the same scale.

One advantage of this last circuit is that the balance is independent of the constants of the vertical coil, and hence, by replacing this coil by others having different numbers of turns the range may be extended indefinitely with only a small change in sensitivity if a valve amplifier (acting as a perfect voltmeter) is used as a detector, since the same fraction of e_2 is always available for balancing purposes.

§ 4. THE DIRECT-READING INSTRUMENT

An improvement will be effected if two scales can be obtained whose readings give the two components directly without further calculation. This can be done by means of the circuit shown in figure 4. The two branches in parallel across AB act as a non-inductive resistance R and, further, the currents in the two branches differ in phase by $\pi/2$ if $L = CR^2$, a condition independent of frequency. If at the normal working frequency the additional condition $L\omega = 1/\omega C = R$ is imposed,

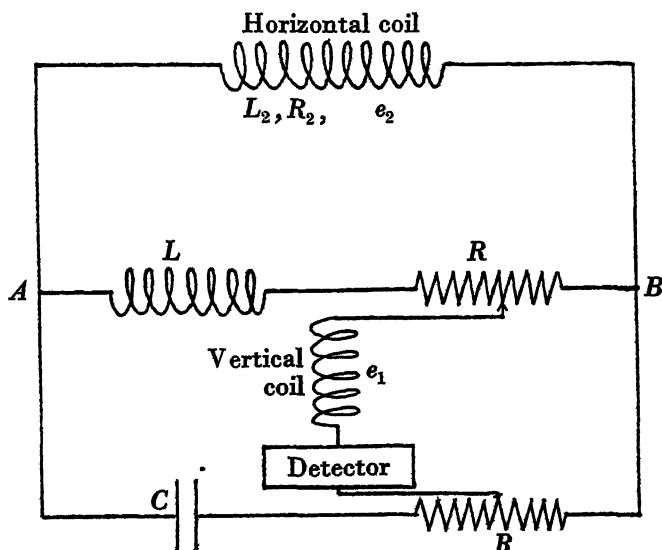


Figure 4.

the two currents will be equal in magnitude and differ in phase from the main current u in the circuit by $\pm \pi/4$. This current is given by

$$u = e_2 / \{R + R_2 + L_2 j\omega\}$$

and if R_2 can be adjusted so that $L_2\omega = R + R_2$, u and e_2 will differ in phase by $\pi/4$. Of the currents in the two branches, one will be in phase and one in quadrature with e_2 ; consequently when the e.m.f. in the vertical coil is balanced, the readings on the two potentiometer scales give direct measures of the in-phase and quadrature components of e_1 . The circuit shown in figure 4 will only allow two quadrants of the (phase, amplitude) diagram to be used, but by making the two potentiometer branches symmetrical this difficulty may be overcome.

§ 5. THEORY OF THE INSTRUMENT

If the e.m.f. in the horizontal coil is e_2 and the corresponding e.m.f. set up in the vertical coil is e_1 , then, with the notation of figure 5, the currents in the various networks are related by the equations

$$\left. \begin{aligned} \{R + R_2 + (L + L_2)j\omega\}.u - (R + Lj\omega).v - (\tfrac{1}{2}R + r + \tfrac{1}{2}Lj\omega).g - e_2 &= 0 \\ - (\tfrac{1}{2}R - r + \tfrac{1}{2}Lj\omega).u + (R - r - s + \tfrac{1}{2}Lj\omega - \tfrac{1}{2}j/\omega C).v - Xg - e_1 &= 0 \\ - (\tfrac{1}{2}R + r + \tfrac{1}{2}Lj\omega).u + (R + r + s + \tfrac{1}{2}Lj\omega - \tfrac{1}{2}j/\omega C).v \\ &\quad + (R + r + s + X + \tfrac{1}{2}Lj\omega - \tfrac{1}{2}j/\omega C).g + e_1 = 0 \end{aligned} \right\} \dots(5),$$

where r and s are the tappings on the potentiometers measured from the central

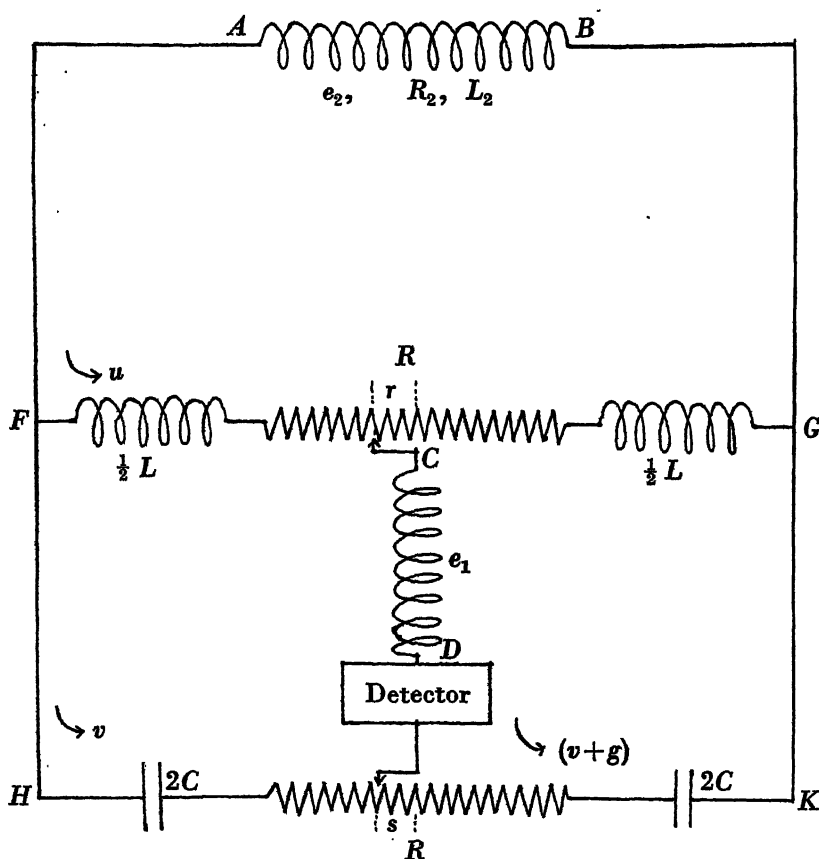


Figure 5.

point and X the impedance of the detector arm. From these, the condition that the current g through the detector shall be zero can be written in the form

$$\begin{aligned} e_1 [\{R + R_2 + (L + L_2)j\omega\} (2R + Lj\omega - j/\omega C) - (R + Lj\omega)^2] \\ = e_2 \{r (R - j/\omega C) - s (R + Lj\omega)\}. \end{aligned}$$

If now $L = CR^2$ then $R + Lj\omega = j\omega CR (R - j/\omega C)$ and hence

$$e_1 \{j\omega CR (R_2 + L_2 j\omega) + R + R_2 + (L + L_2) j\omega\} = e_2 \{r - j\omega CR.s\} \quad \dots\dots(6).$$

The readings r and s will be direct measures of the in-phase and quadrature components of e_1 if the coefficient of e_1 in the above expression is real or imaginary. The condition that the coefficient shall be real cannot be realized, but if

$$R_2 = R (L_2 C \omega^2 - 1)$$

it becomes imaginary and

$$\frac{e_1}{e_2} = - \frac{\omega CR}{\omega (CRR_2 + L + L_2)} \cdot s - j \frac{1}{\omega (CRR_2 + L + L_2)} \cdot r \quad \dots\dots(7).$$

The two readings do not give the two components on the same scale, but this is not important from the practical standpoint, the interpretation of one component being used to supplement the other. The other two scales will be identical if $\omega CR = 1$ in which case

$$L\omega = 1/\omega C = R,$$

$$L_2\omega = R_2 + R$$

and

$$\frac{e_1}{e_2} = - \frac{1}{2(R + R_2)} \cdot (s + jr) \quad \dots\dots(8).$$

For any other frequency the components may be reduced to the same scale by multiplying the in-phase component by ω/ω_0 where $\omega_0/2\pi$ is the frequency at which the scales are equal and $\omega/2\pi$ the applied frequency.

§ 6. SOURCES OF ERROR

(i) *Error due to tilt of search coils.* Since in practice the primary vertical field is much larger than the horizontal field, any slight inclination of the vertical coil will result in a relatively large in-phase flux through the vertical coil. A rotation of the coil system through 180° about a vertical axis will reverse the e.m.f. due to the horizontal field but not that due to the component of the primary field. Consequently the effect of the horizontal field alone may be determined from the two sets of readings and at the same time any induction effect in the leads will be automatically eliminated. Any component of the horizontal field threading the standard coil due to the same cause, will have a negligible effect, the main result being a small phase displacement of e_2 .

(ii) *Error due to e.m.fs. set up in the potentiometer inductances.* A more important error is due to the component of the horizontal field threading the two self-inductances in the potentiometer. The effective areas of the inductances in the instrument constructed in the Royal College of Science were of the order of $2 \cdot 10^4 \text{ cm}^2$, which is about 2 per cent of the effective area of the search coils used in the field (about 10^6 cm^2). If the two induced e.m.f.s are arranged to be equal and to act in opposition in the branch FG , figure 5, it can be shown that the currents in the various nets are given by a set of equations identical with equations (5) except

that e_1 is replaced by $(e_1 - e')$, where e' is the e.m.f. in the inductance. Consequently the instrument will give the components of this quantity, but by reversing the sign of e_1 the unwanted effect e' can be eliminated. The two e.m.f.s can be made equal by having the coils of identical construction and by placing them in parallel planes a short distance apart. Since they are to be joined in opposition their effective inductance is reduced to $(\frac{1}{2}L - M)$, where M is the mutual inductance between them. Consequently the condition that the currents in the two branches shall differ in phase by $\pi/2$ is now

$$L - 2M = CR^2.$$

By using astatically wound inductances the errors due to this source may be reduced to a negligible value and the instrument can be made to have a constant zero.

(iii) *Error due to the self-capacity of the search coils.* To a first approximation the self-capacity of the search coil of inductance L and resistance R may be represented by a condenser C' across its terminals, and it is the potential across this condenser which is measured. If the impedance of the condenser is large compared with the impedance of the coil the error will be small. For an error of less than 1 per cent $\frac{1}{\omega C'} > 100 \{R^2 + L^2 \omega^2\}^{\frac{1}{2}}$. With small coils this error will be negligible but may become important for the larger coils used to measure very small fields. Consequently the error due to the self-capacity of the coil will impose a limit to the lower range of the apparatus.

(iv) *Errors due to residuals in the potentiometer resistances.* If the residual inductances of the two potentiometers are small and equal it can be shown that to the first order of small quantities the two arms in parallel act as a non-inductive resistance R . Hence there is no change in the main current u in the circuit due to this cause. If μ is the reactance per ohm of the potentiometer, and v and w the currents in the two branches then

$$u = e_2 / (R + R_2) (1 + j),$$

$$uR = (R + Lj\omega + j\mu R) \cdot v = (R - j/\omega C + j\mu R) \cdot w$$

or $u = (1 + j + \mu j) \cdot v = (1 - j + \mu j) \cdot w$ at the normal frequency $\omega_0/2\pi$, and

$$e_1 = r (1 + j\mu) \cdot v - s (1 + j\mu) \cdot w;$$

whence, squares of terms involving powers of μ being neglected,

$$\frac{e_1}{e_2} = - \frac{1}{2(R + R_2)} \left[\left\{ s + \frac{\mu}{2} (r - s) \right\} + j \left\{ r - \frac{\mu}{2} (r + s) \right\} \right] \dots\dots(9).$$

The largest value that $(r - s)$ can attain is R , and hence if $\frac{1}{2}\mu R$ (half the residual of the potentiometer resistance) is made less than the smallest tapping on the potentiometer, the residual error will not appear in the measurement and the instrument will remain direct-reading.

(v) *Temperature corrections.* One branch of the potentiometer contains a large fraction of its resistance in the form of copper windings, and since a field instrument of this nature is exposed to a wide range of temperatures, errors will arise as a result

of the variation of resistance with temperature. It can be shown that a change in resistance of δ per cent will produce errors in the measurement of $\delta/4$ per cent, and except for extreme temperatures the errors will be negligible. They may be eliminated entirely with a variable compensating resistance calibrated in temperatures.

(vi) *Error due to change of frequency.* If the instrument has been made direct-reading for the normal working frequency $\omega_0/2\pi$, fluctuations in the frequency of the generator will alter the calibration and errors will be introduced. The general balance condition is given by equation (6) and hence for a frequency $(\omega_0 + \delta\omega)$

$$e_1/e_2 = \{r - j\omega_0 CR (1 + \delta\omega/\omega_0) \cdot s\} / [j\omega_0 CR (1 + \delta\omega/\omega_0) \{R_2 + L_2 j\omega_0 (1 + \delta\omega/\omega_0)\} + R + R_2 + (L + L_2) j\omega_0 (1 + \delta\omega/\omega_0)].$$

Since the instrument is calibrated for the frequency ω_0

$$R = L\omega_0 = 1/\omega_0 C; L_2\omega_0 = R + R_2,$$

if we neglect squares of small quantities the balance condition simplifies to

$$\frac{e_1}{e_2} = -\frac{1}{2(R + R_2)} \left[\left\{ s + r \frac{\delta\omega}{\omega_0} \right\} + j \left\{ r - \frac{\delta\omega}{\omega_0} (r + s) \right\} \right] \quad \dots\dots(10).$$

If the two readings r and s are of the same order of 1 per cent change in the frequency will produce a 2 per cent error in the quadrature component and a 1 per cent error in the in-phase component. The lack of symmetry in the frequency correction is due to the fact that as well as a change in the magnitude of the currents in the two branches there is a phase-displacement of the main current relative to the induced e.m.f.

§ 7. DESCRIPTION OF THE APPARATUS

Two instruments on the principle have been constructed in the workshops of the Royal College of Science, and calibrated and tested in the Applied Geophysics Department. The first was constructed before it was realized that the e.m.f.s induced in the inductances by the alternating magnetic field to be examined would introduce serious error. In the tests the instrument was actually well removed from the magnetic field so that the error could be ignored, but in field practice this would not be possible. The current in these tests was obtained from a petrol-driven generator of the type used in the field, but it was found that the frequency fluctuated so rapidly and in such an erratic manner that the equation (10) could not be applied. As a result the measurements were only accurate to 3 or 4 per cent, owing chiefly to frequency-variations.

Accordingly a second instrument, embodying the design examined above for the compensation of the induced e.m.f.s in the inductances, was constructed. At the same time a synchronous motor was installed to drive the generator, and measurements showed that the frequency was constant to within 1 part in 500. The condensers used in the second instrument were good-quality waxed-paper

condensers* adjusted to values $2.34_2 \mu\text{F.}$ and $2.34_6 \mu\text{F.}$ The inductances were measured at a frequency of 530 c./sec. and had values 38.8_3 mH. and 38.8_1 mH. respectively, and their resistance in series with one another was $24.38 \Omega.$ at 20° C. The total inductance in the circuit was adjusted to 76.8_0 mH. by varying the mutual inductance between the parallel coils. The two $256.0\text{-}\Omega.$ resistances were each composed of a potentiometer of $170 \Omega.$ together with fixed non-inductive resistances to give the correct total. The potentiometers were wound with 30 s.w.g. enamelled Eureka wire on thin strips of cross-section 1.5 cm. by 0.1 mm., each strip being wrapped round a circular former with a rotating arm. Each turn of wire had a resistance of about $0.2 \Omega.$ and subtended an angle of less than half a degree at the centre, so that readings could be made with this accuracy. The calculated inductance of the potentiometer was of the order of 0.05 mH. corresponding to a residual of $0.2 \Omega.$ at the working frequency.

A suitable pair of search coils for field work would consist of a horizontal coil of 200–300 turns on a frame about 60 cm. square, with a vertical coil of approximately the same dimensions. If the vertical coil is tapped so that differing numbers of turns can be employed, the range of the apparatus may be extended. The calibration of the system may be performed by setting R_2 to the value calculated from a knowledge of the frequency, or by a subsidiary horizontal coil in place of the vertical search coil. In the latter case the balance is secured by adjusting R_2 and the in-phase scale, the quadrature scale being set at zero.

§ 8. TEST OF THE APPARATUS

As it was not possible to subject the apparatus to a rigorous field test, field conditions were simulated on a small scale in the laboratory. An elliptically polarized field, whose components could be varied in amplitude and phase, was produced by means of three large loops. Each loop was 7 ft. square, bisected the other two at right angles, and carried a current generally differing in amplitude and phase from the currents in the other two. Consequently the nature of the elliptically polarized field at the centre could be controlled completely. Search coils of much smaller size than those employed in the field were placed at the centre so that the magnetic field at all points in the small volume used in the experiment could be assumed to be spatially uniform. The search coils had diameters of 8 in. and the calculated magnetic field was uniform to within 2 per cent. The horizontal search coil with 530 turns of wire had an inductance of 92.7 mH. and effective area of $1.97 \times 10^5 \text{ cm}^2$, while the vertical coil of 15 mH. had an effective area of $7.5 \times 10^4 \text{ cm}^2$. Their self-capacities were less than $0.003 \mu\text{F.}$, and hence the errors due to this cause may be neglected. The balance readings were obtained by using a resistance-capacity-coupled valve amplifier as the detector, with a filter circuit in the output to reduce the effect of harmonics.

* In the original instrument these were mica condensers supplied by the Radio Research Board, Slough, through the courtesy of the Department of Scientific and Industrial Research. They were replaced by waxed-paper condensers to reduce the weight of a field instrument.

The circuit used to produce the magnetic field is shown in figure 6. The loops were made with aluminium-armoured wire with the covering earthed. The loops and the search coils virtually constitute a screened transformer in which capacity currents are reduced to a minimum, but the effective current will differ from the core current on account of the eddy currents set up in the shield. Since this is the same for all loops, then if I_1 , I_2 and I_3 are the currents in the three loops

$$I_1 r_1 = I_2 r_2 = -jI_3 / \omega K$$

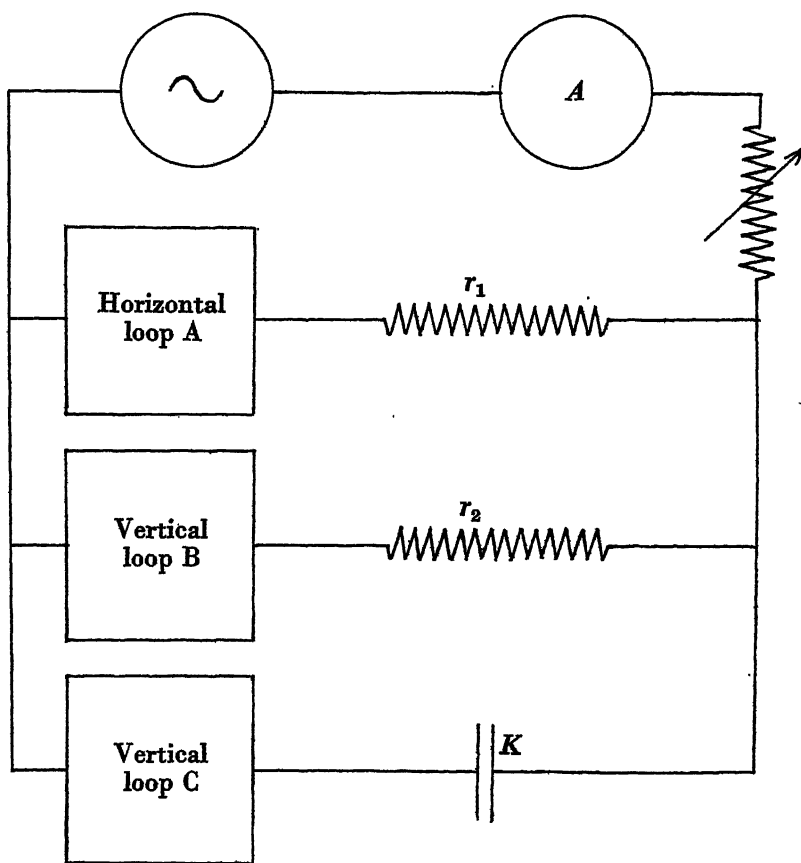


Figure 6.

or since the magnetic fields are proportional to the currents,

$$Zr = Xr_2 = -jY/\omega K \quad \dots\dots(11),$$

where Z is the vertical and X and Y the two horizontal components of the field. Hence X and Z are in phase and Y and Z are in quadrature, while X and Y , besides being in quadrature, differ in direction by 90° , since the coils producing them are at right angles. The test consisted of measuring X and Y in terms of Z to see if the instrumental readings satisfied the above conditions.

It was found impossible to make the test directly on account of the residual field due to the leads to the loops and the phase-splitting device; moreover, under these conditions the apparatus could not be calibrated experimentally. Hence R_2 was set to the calculated value for the frequency used. With the horizontal loop permanently in the circuit, the horizontal field was measured for various azimuths of the vertical search coil. The tests consisted of the following operations. (a) Measurement of residual field R . (b) Measurement of the combined field of R and field X due to B . (c) Measurement of the combined field of R and field Y due to C . (d) Measurement of the combined field of R and the fields due to B and C . The balances obtained were sharp and could be recovered to within half a scale-division.

In all cases it was found that the horizontal field could be represented by an equation of the type

$$\alpha = a + b \cos (\theta + \delta)$$

where θ is the azimuth of the vertical coil and α the measure of the component in terms of the scale-readings on the potentiometer. The first term is the error (i) discussed on p. 357, while the second is the contribution of the horizontal field. From readings $\alpha_1, \alpha_2, \alpha_3$ obtained in azimuths $\theta, (\theta + 120)$ and $(\theta + 240)$ the three constants may be calculated.

$$a = \frac{1}{3} (\alpha_1 + \alpha_2 + \alpha_3)$$

$$b = \frac{1}{3} \{3 (\alpha_2 - \alpha_3)^2 + (\alpha_2 + \alpha_3 - 2\alpha_1)^2\}^{\frac{1}{2}}$$

$$\delta = \tan^{-1} \{(\alpha_2 - \alpha_3) \sqrt{3} / (\alpha_2 + \alpha_3 - 2\alpha_1)\} - \theta.$$

A typical set of readings illustrating the accuracy which can be obtained will now be given.

Measurement of total field (vector sum of R, X and Y).

$$r_1 = 5.55 \Omega, r_2 = 10.09 \Omega, K = 10.2 \mu F., 1/\omega K = 29.3 \Omega.$$

$$\text{Total current, } 2.56 \text{ A. Frequency, } 533 \text{ c./sec.}$$

Azimuth θ	Readings at			a	b	$(\theta + \delta)$ (degrees)	δ (degrees)
	θ	$(\theta + 120)$	$(\theta + 240)$				
In-phase component							
0°	154	— 98	— 54	0.7	154.6	9.9	9.9
30°	120.5	— 145	26	0.5	154.9	39.4	9.4
60°	55	— 151	99.5	1.2	154.5	69.6	9.6
90°	— 23.5	— 117.5	146.5	1.8	154.5	99.4	9.4
			Mean	1.0	154.5	—	9.6
Quadrature component							
0°	— 54.5	— 61.5	116.5	+ 0.2	116.2	— 62.0	— 62.0
30°	— 97.5	— 3.5	102	+ 0.3	115.2	— 31.9	— 61.9
60°	— 116.5	55	61	— 0.2	116.2	— 1.9	— 61.9
90°	— 102.5	99	3.5	—	116.3	28.3	— 61.7
			Mean	—	116.0	—	— 61.9

One division corresponds to a ratio of $|e_1/e_2|$ equal to $8.80 \cdot 10^{-4}$ on the in-phase scale and to $8.60 \cdot 10^{-4}$ on the quadrature scale. The in-phase and quadrature

components of the fields being denoted by the suffixes i and q , the equations representing the horizontal fields for the above current-distribution were

$$\left. \begin{aligned} R_i &= 1 - 91 \cos (\theta - 14.4^\circ) \\ R_q &= -55.5 \cos (\theta - 19.1^\circ) \end{aligned} \right\} \dots\dots(a),$$

$$\left. \begin{aligned} R_i + X_i &= 1 + 155.5 \cos (\theta + 9.5^\circ) \\ R_q + X_q &= -55.5 \cos (\theta - 18.8^\circ) \end{aligned} \right\} \dots\dots(b),$$

$$\left. \begin{aligned} R_i + Y_i &= 1 - 90.5 \cos (\theta - 14^\circ) \\ R_q + Y_q &= -117 \cos (\theta - 62.3^\circ) \end{aligned} \right\} \dots\dots(c),$$

$$\left. \begin{aligned} R_i + X_i + Y_i &= 1 + 154.5 \cos (\theta + 9.6^\circ) \\ R_q + X_q + Y_q &= -116 \cos (\theta - 61.9^\circ) \end{aligned} \right\} \dots\dots(d).$$

From equations (a), (b) and (c) we derive

$$\left. \begin{aligned} R_i + X_i + Y_i &= 1 + 155.5 \cos (\theta + 9.1^\circ) \\ R_q + X_q + Y_q &= -117 \cos (\theta - 62.2^\circ) \end{aligned} \right\} \dots\dots(e),$$

which are in good agreement with the measured values (d). The two fields due to the vertical loops B and C are, from the above equations, given by

$$\left. \begin{aligned} X_i &= 241.5 \cos (\theta + 0.6^\circ) \\ X_q &= 0.5 \cos (\theta + \gamma_1) \\ Y_i &= 0.5 \cos (\theta + \gamma_2) \\ Y_q &= 85.5 \cos (\theta + 91.3^\circ) \end{aligned} \right\}.$$

Of these, the quadrature component X_q^* is small compared with X_i while the in-phase component Y_i is small compared with Y_q . Hence the field due to B is in phase with that due to A and in quadrature with that due to C . Further, the angle between the two fields is 90.7° .

The ratios of the amplitudes of the various fields may be calculated from the known current-distribution by means of equation (11), and also from the scale-values of the instrument-readings. The results for the experiments quoted are as follows.

Ratio	Z/X	Y/X
Calculated from current-distribution	1.82	0.345
Calculated from instrument readings	1.81	0.346

Hence the fields as measured by the instrument agree well with the fields calculated from the known current-distribution in the loops quantitatively as well as qualitatively.

The effect of an external field on the instrument itself was examined also to determine if the compensation of the e.m.f.s set up in the potentiometer inductances was sufficient. The field in which the instrument was placed was produced by two subsidiary square coils of side 92 cm. separated by a distance of 50.2 cm. This separation is the most favourable for producing a minimum variation of the field

* The terms X_q , Y_i are small differences between large quantities and it is doubtful if the figures have any real significance. For this reason γ_1 and γ_2 are not given.

parallel to the axis over a plane midway between the coils*. With the search coils in a fixed position in the system for producing an elliptically polarized field, the measuring instrument was moved into the magnetic field produced by the subsidiary coil system with the two inductances symmetrically on either side of the mid-plane. The readings representing the ratio of the fields threading the search coils were found to agree among themselves within 0.5 per cent, although the induced e.m.f.s in the inductances produced zero-shifts of from 0 to 50 divisions on one scale, and from 0 to 20 divisions on the other. The displacement of the zero, which is a measure of the magnetic fields threading the inductances, when plotted against the position of the instrument in the magnetic field followed closely the transverse variation of a magnetic field due to the square-coil system. Further, it was found that if the inductances were placed in unequal fields the instrument readings no longer agreed with the values obtained when the instrument was in zero field. Consequently the compensation is not perfect unless the inductances are in equal fields.

§ 9. ACKNOWLEDGMENTS

In conclusion, I wish to thank Prof. A. O. Rankine for the interest he has shown in this work; and the Department of Scientific and Industrial Research for the financial assistance which rendered it possible.

* A. O. Rankine, "Presidential Address to the Physical Society," *Proc. Phys. Soc.* 46, 1 (1934).

NOTE ON INTEGRALS OF PRODUCTS OF EXPERIMENTALLY DETERMINED MAGNITUDES

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ABSTRACT. The integral of a product of quantities known only for discrete values of a variable is given correctly by the simple sum of the products for uniformly distributed values of the variable. Nothing is gained by increasing the number of component products beyond the number of observed values of either factor.

A PROBLEM which may arise in various branches of physics may be illustrated by an optical example. It is desired to find the luminosity of the light from a given source transmitted by a filter as evaluated by a "standard observer." The quantity required is

$$\int etv d\lambda$$

taken over the whole visible spectrum, where e represents the energy of the source, t is the transmission factor of the filter, and v is the visibility function by which the standard observer is defined, all expressed as functions of the wave-length λ . Of these magnitudes only e is in any case known precisely for all wave-lengths. The value of t will be determined to a certain accuracy for discrete wave-lengths spread over the spectrum, and v is also defined by a table of numbers for discrete wave-lengths only. For the integral to have a meaning it is necessary to suppose that when any factor is not a known continuous function of the wave-length we are to understand by the symbol a continuous function of simple type which assumes the known values for definite wave-lengths. In effect this means that these factors will be regarded as polynomials in which the coefficients may change with the wave-length. The changes in the coefficients are due to the adoption of polynomials of much lower order than the number of wave-lengths for which the functions are defined. In consequence of this change, and of the substitution of summation for integration, the value found for the integral will vary with the detailed procedure adopted. For example the result obtained by interpolating values of the product according to a given rule will differ from that consequent on applying the same interpolation rule to the individual factors of the product. If the wave-length subdivision is sufficiently close the range over which the integral can vary will be without real significance. On the other hand the labour of experimental observation and subsequently that of computation are directly proportional to the number of terms involved in the sum. It is thus important to know on what these variations depend, and to determine what procedure yields an answer, free from errors exceeding a selected value, with the least expenditure of labour.

In optical problems it most frequently happens that the integrand consists effectively of two factors. In the example given e is much more frequently than not the energy emitted by a standard source, and the product ev is then tabulated. It is quite sufficient for the discussion of the problem to consider only two factors. The extension to a greater number of factors can readily be made if desired by treatment similar to that given here.

We suppose then that the integrand a is the product of two factors b and c which are only known for positive and negative integral values of the variable x over the range for which integration is to be made. For all values of x outside this range we ascribe the value zero to one at least of the factors b, c . In the neighbourhood of any particular integral value of x , which we may without loss of generality suppose to be $x = 0$, we may represent b and c by polynomials in x . If we represent by α, β, γ the central difference operators defined by the equations

$$\begin{aligned} 4\alpha a_p &= a_{p+1} - 2a_p + a_{p-1} = b_{p+1}c_{p+1} - 2b_p c_p + b_{p-1}c_{p-1} \\ 4\beta b_p &= b_{p+1} - 2b_p + b_{p-1} \\ 4\gamma c_p &= c_{p+1} - 2c_p + c_{p-1}, \end{aligned}$$

where p is zero or a positive or negative integer, the polynomial of order $2n$ representing b in the neighbourhood of $x = 0$ determined from its $2n + 1$ values $b_n, b_{n-1}, \dots, b_{-n}$ is

$$\begin{aligned} b &= \left\{ 1 + \frac{x^2}{2!} 4\beta + \frac{x^2(x^2 - 1^2)}{4!} (4\beta)^2 + \frac{x^2(x^2 - 1^2)(x^2 - 2^2)}{6!} (4\beta)^3 + \dots \right\} b_0 \\ &\quad + \frac{1}{2} \left\{ x + \frac{x(x^2 - 1^2)}{3!} 4\beta + \frac{x(x^2 - 1^2)(x^2 - 2^2)}{5!} (4\beta)^2 + \dots \right\} (b_1 - b_{-1}), \end{aligned}$$

where the series in the first bracket terminates after $n + 1$ terms and that in the second after n terms, and a similar expression holds for c . This is merely one form of the familiar Lagrangian interpolation formula, as may be verified on inspection. We can thus express the integrand as a polynomial in x of order $4n$, where the coefficients are the values of b and c for integral values of x , and we are assuming that each factor is to be interpolated separately. Now in every interval the integral is of the form

$$\int_{-\xi}^{\xi} bc \, dx,$$

where ξ is the same for all the intervals. Clearly the contribution of odd powers of x in the product bc is zero. We may accordingly reject in bc all terms with odd powers of x , and take as the integrand

$$\begin{aligned} &\left\{ 1 + \frac{x^2}{2!} 4\beta + \frac{x^2(x^2 - 1^2)}{4!} (4\beta)^2 + \dots \right\} \left\{ 1 + \frac{x^2}{2!} 4\gamma + \frac{x^2(x^2 - 1^2)}{4!} (4\gamma)^2 + \dots \right\} b_0 c_0 \\ &\quad + \frac{x^2}{4} \left\{ 1 + \frac{x^2 - 1^2}{3!} 4\beta + \dots \right\} \left\{ 1 + \frac{x^2 - 1^2}{3!} 4\gamma + \dots \right\} (b_1 - b_{-1})(c_1 - c_{-1}). \end{aligned}$$

Also

$$\begin{aligned} (b_1 - b_{-1})(c_1 - c_{-1}) &= 2(b_1 c_1 - 2b_0 c_0 + b_{-1} c_{-1}) - 2(b_1 - 2b_0 + b_{-1}) c_0 \\ &\quad - 2b_0 (c_1 - 2c_0 + c_{-1}) - (b_1 - 2b_0 + b_{-1})(c_1 - 2c_0 + c_{-1}) \\ &= 8(\alpha - \beta - \gamma - 2\beta\gamma) b_0 c_0, \end{aligned}$$

so that all the coefficients in the integral, apart from the term $b_0 c_0$ itself, involve the central differences of b_0 , c_0 or $b_0 c_0$. The integral may therefore be evaluated by applying certain factors to the sums of terms involving these central differences. If however the central differences are themselves of suitably small magnitude all sums in which they appear will be negligible, and the integral itself will then be accurately determined by the simple sum $\Sigma b_p c_p$. The lowest order of the central differences which appear as a correction to this sum is clearly a matter of interest. Since β and γ act on different factors it is obvious that these operations are commutable for multiplication. If we extend the definition of α and define a new operator δ in accordance with the equations

$$\begin{aligned} 4\alpha b_p c_q &= b_{p+1} c_{q+1} - 2b_p c_q + b_{p-1} c_{q-1} \\ 4\delta b_p c_q &= b_{p+1} c_{q-1} - 2b_p c_q + b_{p-1} c_{q+1}, \end{aligned}$$

it is clear, since the operators only involve differencing and additions to suffixes, that we may commute the order of any of the operators α , β , γ , δ in products. It is also easy to verify that

$$(\beta - \gamma)^2 b_p c_q = \alpha \delta b_p c_q.$$

Moreover, from the definition of α it follows that on summation any expression including the operator α as a factor vanishes if the operand vanishes at the limits of summation. In evaluating the integral we may therefore reject all terms involving α , and by the relation just given also all terms containing $(\beta - \gamma)^2$ as an operator.

Now, apart from $b_0 c_0$, the terms of lowest order in the expansion of a in powers of β and γ are

$$\left\{ \frac{x^2}{2!} 4(\beta + \gamma) - \frac{x^2}{4} 8(\beta + \gamma) \right\} b_0 c_0,$$

and vanish identically. Those of the next order are found to be

$$\frac{4x^2(x^2 - 1^2)}{3!} \{2\alpha(\beta + \gamma) - (\beta - \gamma)^2\} b_0 c_0,$$

and therefore vanish on summation. This result suggests that when differences of all orders are taken into account all the terms except the first may disappear on summation. To investigate this we note that if we write ϕ , $\sinh^2 \theta$ and $\sinh^2 \phi$ for α , β and γ respectively the effective operator acting on $b_0 c_0$ is represented by

$$\begin{aligned} \cosh 2x\theta \cosh 2x\phi - 2 \sinh 2x\theta \sinh 2x\phi (\sinh^2 \theta + \sinh^2 \phi \\ + 2 \sinh^2 \theta \sinh^2 \phi) / \sinh 2\theta \sinh 2\phi \end{aligned}$$

or by
$$\frac{\cosh 2x(\theta - \phi) \sinh^2(\theta + \phi) - \cosh 2x(\theta + \phi) \sinh^2(\theta - \phi)}{\sinh 2\theta \sinh 2\phi}$$

from which it is clear that every term of the expansion involving x contains $(\beta - \gamma)^2$ as a factor, and thus vanishes on summation. It follows that any departure of the integral from the value $\Sigma b_p c_p$ is attributable to the termination of the series occurring in the integrand, i.e. to approximations in the interpolation differing from the best values obtainable. The correct value of the integral must therefore be taken to be $\Sigma b_p c_p$, and any attempts to improve accuracy by finding intermediate values of the integrand introduce errors when the change is not precisely nil.

It will be noted that no attention has been paid to the value to be given to ξ . The result just reached shows that this is unnecessary, and also removes all formal difficulties which require consideration when brief interpolation formulae are applied, such as discontinuities in the function, or in its differential coefficients, when x differs from an integer by ξ .

The fundamental assumption upon which this simple conclusion rests is that interpolation is effected by a symmetrical Lagrangian formula. We have taken as an illustration the case when the number of given points is odd, but the modifications needed when the number is even are slight and readily made. It follows that interpolation of a different type in problems of this kind should not be substituted for the Lagrangian unless this is justified by special considerations.

In practice it will often happen that observations are not available for uniformly distributed values of one of the variables. For instance the transmission factor of a filter might conceivably be obtained for certain wave-lengths of a line spectrum. The correct procedure is then to construct a Lagrangian expression for the given observations and evaluate the transmission from this for a series of uniformly distributed points.

There is only one case in which there is any need to subdivide any of the standard intervals. This is when the values of the observed magnitude (represented by c say) are not adequately defined by their values at the standard points. An extreme example is afforded by a function which is zero at these points and is positive elsewhere. The best procedure is then to subdivide the standard interval only where and only to the extent it is necessary to secure a proper representation of the function measured, to interpolate by the Lagrangian method for the sub-intervals, and to separate the integral into two parts as considered in the following argument.

Let the whole range of integration be represented by $ABCD$, BC being the region where it is essential to subdivide the standard intervals. We can divide c into two parts c_1 and c_2 , c_1 being equal to c outside the range BC , and being defined within the range BC precisely by its values at the standard intervals. Under these conditions if we write $a_1 = bc_1$, $a_2 = bc_2$, we obtain exactly the same value for the a_1 sum whether we take the larger or the smaller intervals, and this value is equal to $\int_A^D a_1 dx$. Again a_2 is a function by hypothesis accurately defined by its values at the smaller intervals within the range BC , and vanishing outside this range. Hence

$$\int_A^D a_2 dx = \int_B^C a_2 dx$$

and both are equal to the a_2 sum for the smaller intervals. Also

$$\int_A^D a dx = \int_A^D a_1 dx + \int_A^D a_2 dx$$

and the total sum therefore represents the integral correctly.

To determine the a_2 sum we clearly have to interpolate b for the intermediate points in BC , and also to interpolate c_1 within this interval in order to obtain c_2 by

subtraction from c . In practice this work will be light, for in subintervals the changes in b and c_1 will tend to be simple in character. In obtaining the a_2 sum care must be taken not to omit division by the number representing the ratio in which the intervals have been increased, which takes proper account of the reduced value of the new intervals.

From this discussion it immediately follows that there is no point in evaluating an integral by summing more terms than there are observed values of either factor in the integrand. For example, if observations are made on c corresponding only to alternate entries of the standard function b , it will be better to construct an equivalent b table for the larger intervals than to interpolate c for the standard intervals. By the theory just considered it is apparent that the new b table can be constructed to give exactly the same result as precise interpolation of c would yield, but the labour involved is reduced to less than a half. The work involved in constructing the new table is comparable with that required for a single interpolation of the factor c for the complete range. It is clearly advantageous to construct tables for all the observation intervals in regular use.

DISCUSSION

Mr J. GUILD. This paper deals with a type of problem which arises in most branches of experimental physics. Integration of a product of two or more quantities each of which is a function of some variable (wave-length in the example chosen) is of frequent occurrence, and the experimental information concerning the various functions is very often available only for a discrete series of values of the variable. There are interesting questions of principle involved in the status of interpolated values of a quantity when (a) the quantity in question has no existence except as *defined* by its values at specified values of the variable, as in the case of the various quantities, such as v_λ in the author's example, defining the hypothetical "standard observer"; and (b) when the quantity is a real physical quantity, such as energy, or the transmission of a filter (e_λ and t_λ in the author's example) which is defined independently of the variable with respect to which interpolation is carried out, and which possesses an actual value at any value of the variable whether we know what it is or not. These questions would carry us outside the reasonable scope of this discussion: I only mention that they exist, because there is a tendency among some physicists to assume that mathematical considerations can lead to principles of interpolation which will obtain, from a discrete series of observations of a physical quantity, the physically correct values at intermediate points, and it is necessary always to bear in mind that any process of interpolation, applied to physical quantities, necessarily yields only an approximation—it is a make-shift device for getting certain information from inadequate data. Interpolation can never be regarded as a formal substitute for a complete statement of the physical facts, where such physical facts exist as in the cases coming under (b); whereas it can be regarded as a formal substitute for a more extensive definition of quantities coming under (a), for which no independent physical facts exist.

Mr Smith does not draw this distinction in the paper, but treats the interpolates of e and t (or their product) as having the same significance as those of v . In practice, of course, this must be done, since the problem is, by hypothesis, how best to proceed when one is ignorant of the intermediate values of the physical quantities, and our actual procedure cannot be affected by the existence or non-existence of true values which are, in any case, outside our knowledge. The importance of the distinction is simply in the significance we attach to the result to which the procedure leads.

Mr Smith's procedure is, in effect, to extend the *definition* of the standard observer so that it includes a Lagrangian interpolation formula as defining values of v_λ between the tabulated values, and to *assume* that the variation of the physical quantity $e_\lambda t_\lambda$ between the observed values will also be in accordance with this formula. From these premises he obtains two results of great practical importance, which, as far as I am aware, have not been stated before and which are certainly not generally known, namely, that the correct value of the integral is simply the sum of the products of the various factors at the discrete (equally spaced) values of the variable for which their values are known, and that there is no point in evaluating an integral by summing more terms than there are observed values of any of the factors in the integrand.

Applied to practical problems the first conclusion must be regarded as approximate, inasmuch as we have no guarantee that the actual intermediate values of the physical factors are correctly represented by Lagrangian interpolation. This of course is shown by the examples illustrating the author's next paper, in which the results obtained by applying these formulae over two different ranges of interpolation, though agreeing very closely, do not agree exactly.

It must, nevertheless, be regarded as the best value obtainable from a given set of data, because although we know that the Lagrangian formula is almost certainly inaccurate in any particular case, we have absolutely no reason for expecting the unknown facts to be better represented by any other formula. There is therefore nothing we can do with the data which will reduce the uncertainty of the result, and Mr Smith's second conclusion "that there is no point etc. . . ." is universally true whatever may be the actual (but by hypothesis unknown) values of the quantities between the observed points. I have before now gone to great trouble to interpolate between observed spectrophotometric values in order to get what I hoped would be a more reliable value for the integral photometric transmission, or the colour coordinates of a filter, and doubtless others have done the same. Clearly this is pure waste of labour and adds nothing to the reliability of the result, which can only be improved, when improvement is necessary, by diminishing the interval at which experimental observations are made.

AUTHOR'S reply. I agree with Mr Guild on the importance of realizing the precise significance of the procedure followed in calculations, but I am not sure that our views on some of the points he refers to are in complete agreement though I think we should agree up to the point where the question becomes only of theo-

retical interest. There is no doubt that any finite continuous function representing physical magnitudes or the mathematical functions needed by the physicist can be represented over any conveniently short range of a variable by a polynomial with an error not exceeding an arbitrarily assigned small but finite value, and unless the physical magnitudes are of this character an integral involving them has no meaning. As the observational intervals are reduced the possible range of variation of the function within the interval is reduced continuously also, and the two tend to zero together. In any case in which this did not occur I should incline to the view that the variations represented experimental errors, and take smoothed values rather than the irregular observations as the proper representation of the magnitude. That is to say there is a point beyond which I should not admit that data were inadequate or the smooth function an approximation. I can see no possible ultimate escape from reliance upon interpolation for physical magnitudes in problems of this kind. From their very nature the complete statement of the physical facts in the sense I think Mr Guild means is always impossible, so that some such view as the one I have given is necessary if we are to deal with physical measurements in this connexion at all. If then we leave on one side, as we must, all questions of the adequacy of particular sets of data, we have only to consider the relative advantages and conveniences of polynomials constructed in various ways (all of which may represent the data within given limits), e.g. whether we should use an expression of a particular order, and whether we ought to secure osculatory contact where the sections meet. In view of the result reached in this paper with the formula first considered there is no point in discussing any other.

It ought to be particularly remembered that the conclusions reached in this paper depend upon the assumption that the integrand vanishes for an indefinitely long range of the variable at either end of the region for which it differs from zero. It is for this reason that we obtain, on replacing one of the factors by unity, a formula differing from the well-known expressions for evaluating areas exemplified by Simpson's and Weddle's rules; in these it is assumed that nothing is known of the function outside the range of integration.

(Discussion continued on page 478)

Proc. Phys. Soc. 46, 371, 378 (1934).

Transpose the words

(Discussion continued on page 478)

from page 371 to page 383.

CONDENSED TABLES FOR COLOUR COMPUTATION

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ABSTRACT. It is sometimes sufficient in the spectrophotometry of coloured materials for the determination of their colour coordinates on the C.I.E. system to take measurements at intervals of $10\text{ m}\mu$. instead of the standard interval of $5\text{ m}\mu$. Special tables have been computed for use in these cases which give with less labour results indistinguishable from those which would be obtained from the use of the standard observer tables.

THE C.I.E. system for the specification of colours has been discussed at some length in the *Transactions of the Optical Society**. In addition to the specification of scales on which colour coordinates are to be expressed that system specifies some standard illuminants for colorimetry and also a standard observer. The most precise specification of a colour is obtained by accurate and adequate spectrophotometry followed by computation utilizing the tabulated properties of the standard observer. By adequate spectrophotometry is to be understood measurement at wave-length intervals small enough to represent the transmissive or other properties of the material examined with accuracy over the whole visible spectrum. Since the standard tables proceed by intervals of $5\text{ m}\mu$. it will be understood that for the general run of sources and materials measurements at these intervals will suffice. This of course does not imply that there are not unusual cases in which measurement at still smaller intervals is needed: when this occurs intermediate values in the standard observer tables will have to be interpolated; it is not then necessary to specify the interpolation formula to be used since the tabulated values are close enough for significant variations not to arise.

Of greater importance than the reduction of intervals is the problem of extending the intervals and so reducing the amount of observational work as well as of computation needed to obtain a correct result. Experience shows that the spectral properties of many materials are adequately described by their values at intervals of $10\text{ m}\mu$. The formally correct procedure when this is known to be true is then to measure at the $10\text{ m}\mu$. intervals, to interpolate values for the $5\text{ m}\mu$. intervals by a suitable formula, and then to compute exactly as though observations had been made at the $5\text{ m}\mu$. intervals. It is possible however to obtain the same result with less labour by constructing special tables to replace the standard tables *under these special circumstances only*. It has been shown elsewhere† in this volume that we

* The C.I.E. Colorimetric Standards and their Use. *Trans. Opt. Soc.* 33, 73 (1931-2).

† Page 365.

Table 1

Equal energy stimulus			Wave-length (m μ .)	Standard illuminant A		
\bar{x}	\bar{y}	\bar{z}		$E\bar{x}$	$E\bar{y}$	$E\bar{z}$
0.0023	0.0000	0.0106	380	0.0010	0.0000	0.0048
0.0082	0.0002	0.0391	390	0.0046	0.0001	0.0219
0.0283	0.0007	0.1343	400	0.0193	0.0005	0.0916
0.0840	0.0023	0.4005	410	0.0688	0.0019	0.3281
0.2740	0.0082	1.3164	420	0.2666	0.0080	1.2811
0.5667	0.0232	2.7663	430	0.6479	0.0265	3.1626
0.6965	0.0458	3.4939	440	0.9263	0.0609	4.6469
0.6730	0.0761	3.5470	450	1.0320	0.1167	5.4391
0.5824	0.1197	3.3426	460	1.0207	0.2098	5.8584
0.3935	0.1824	2.5895	470	0.7817	0.3624	5.1445
0.1897	0.2772	1.6193	480	0.4242	0.6198	3.6207
0.0642	0.4162	0.9313	490	0.1604	1.0398	2.3266
0.0097	0.6473	0.5455	500	0.0269	1.7956	1.5132
0.0187	1.0077	0.3160	510	0.0572	3.0849	0.9674
0.1264	1.4172	0.1569	520	0.4247	4.7614	0.5271
0.3304	1.7243	0.0841	530	1.2116	6.3230	0.3084
0.5810	1.9077	0.0408	540	2.3142	7.5985	0.1625
0.8670	1.9906	0.0174	550	3.7329	8.5707	0.0749
1.1887	1.9896	0.0077	560	5.5086	9.2201	0.0357
1.5243	1.9041	0.0042	570	7.5710	9.4574	0.0209
1.8320	1.7396	0.0032	580	9.7157	9.2257	0.0170
2.0535	1.5144	0.0023	590	11.5841	8.5430	0.0130
2.1255	1.2619	0.0016	600	12.7103	7.5460	0.0096
2.0064	1.0066	0.0007	610	12.6768	6.3599	0.0044
1.7065	0.7610	0.0003	620	11.3577	5.0649	0.0020
1.2876	0.5311	0.0000	630	8.9999	3.7122	0.0000
0.8945	0.3495	0.0000	640	6.5487	2.5587	0.0000
0.5681	0.2143	0.0000	650	4.3447	1.6389	0.0000
0.3292	0.1218	0.0000	660	2.6234	0.9706	0.0000
0.1755	0.0643	0.0000	670	1.4539	0.5327	0.0000
0.0927	0.0337	0.0000	680	0.7966	0.2896	0.0000
0.0457	0.0165	0.0000	690	0.4065	0.1467	0.0000
0.0225	0.0081	0.0000	700	0.2067	0.0744	0.0000
0.0117	0.0042	0.0000	710	0.1108	0.0398	0.0000
0.0057	0.0020	0.0000	720	0.0556	0.0195	0.0000
0.0028	0.0010	0.0000	730	0.0280	0.0100	0.0000
0.0014	0.0006	0.0000	740	0.0144	0.0062	0.0000
0.0006	0.0002	0.0000	750	0.0063	0.0021	0.0000
0.0003	0.0001	0.0000	760	0.0032	0.0011	0.0000
0.0001	0.0000	0.0000	770	0.0011	0.0000	0.0000
21.3713	21.3714	21.3715	Totals	109.8450	100.0000	35.5824

Table 1 (continued)

Standard illuminant B			Wave-length (m μ .)	Standard illuminant C		
<i>E\bar{x}</i>	<i>E\bar{y}</i>	<i>E\bar{z}</i>		<i>E\bar{x}</i>	<i>E\bar{y}</i>	<i>E\bar{z}</i>
0.0025	0.0000	0.0113	380	0.0036	0.0000	0.0164
0.0123	0.0003	0.0585	390	0.0183	0.0004	0.0870
0.0558	0.0014	0.2650	400	0.0841	0.0021	0.3992
0.2091	0.0057	0.9970	410	0.3180	0.0087	1.5159
0.8274	0.0248	3.9750	420	1.2623	0.0378	6.0646
1.9793	0.0810	9.6617	430	2.9913	0.1225	14.6019
2.6889	0.1768	13.4883	440	3.9741	0.2613	19.9357
2.7460	0.3105	14.4729	450	3.9191	0.4432	20.6551
2.4571	0.5050	14.1020	460	3.3668	0.6920	19.3235
1.7297	0.8018	11.3825	470	2.2878	1.0605	15.0550
0.8629	1.2609	7.3655	480	1.1038	1.6129	9.4220
0.2960	1.9190	4.2939	490	0.3639	2.3591	5.2789
0.0437	2.9133	2.4552	500	0.0511	3.4077	2.8717
0.0810	4.3669	1.3694	510	0.0898	4.8412	1.5181
0.5405	6.0602	0.6709	520	0.5752	6.4491	0.7140
1.4555	7.5959	0.3705	530	1.5206	7.9357	0.3871
2.6899	8.8322	0.1889	540	2.7858	9.1470	0.1956
4.1838	9.6060	0.0840	550	4.2833	9.8343	0.0860
5.8385	9.7722	0.0378	560	5.8782	9.8387	0.0381
7.4723	9.3341	0.0206	570	7.3230	9.1476	0.0202
8.8406	8.3947	0.0154	580	8.4141	7.9897	0.0147
9.7329	7.1777	0.0109	590	8.9878	6.6283	0.0101
9.9523	5.9086	0.0075	600	8.9536	5.3157	0.0067
9.4425	4.7373	0.0033	610	8.3294	4.1788	0.0029
8.1290	3.6251	0.0014	620	7.0604	3.1485	0.0012
6.2135	2.5629	0.0000	630	5.3212	2.1948	0.0000
4.3678	1.7066	0.0000	640	3.6882	1.4411	0.0000
2.8202	1.0638	0.0000	650	2.3531	0.8876	0.0000
1.6515	0.6110	0.0000	660	1.3589	0.5028	0.0000
0.8796	0.3223	0.0000	670	0.7113	0.2606	0.0000
0.4602	0.1673	0.0000	680	0.3657	0.1329	0.0000
0.2218	0.0801	0.0000	690	0.1721	0.0621	0.0000
0.1065	0.0384	0.0000	700	0.0806	0.0290	0.0000
0.0538	0.0193	0.0000	710	0.0398	0.0143	0.0000
0.0253	0.0089	0.0000	720	0.0183	0.0064	0.0000
0.0120	0.0043	0.0000	730	0.0085	0.0030	0.0000
0.0058	0.0025	0.0000	740	0.0040	0.0017	0.0000
0.0024	0.0008	0.0000	750	0.0017	0.0006	0.0000
0.0012	0.0004	0.0000	760	0.0008	0.0003	0.0000
0.0004	0.0000	0.0000	770	0.0003	0.0000	0.0000
99.0915	100.0000	85.3094	Totals	98.0699	100.0000	118.2216

cannot improve the accuracy of the integral of a product by interpolation between observed values of a factor. If both factors of the product are smooth to a very high order we obtain the best result by summing the products for the observed intervals. It follows that if the properties of the standard observer were smooth to a very high order we could not do better than simply employ the tabulated values corresponding to the wave-lengths for which observations have been made and form our sums without more ado. In fact the standard observer properties are smooth enough for the outstanding irregularities to produce no difference that could be appreciated in any tests that have so far been made at the National Physical Laboratory, but they do not formally satisfy the conditions to the highest order that might be considered. It has therefore been thought desirable to construct special tables which meet this condition fully.

That the problem can be solved by the construction of special tables is easily seen. Let b represent an entry in the tables specifying the standard observer, and c the corresponding experimentally determined quantity, for instance the transmission factor of a filter for the wave-length to which b refers. The quantity to be found is Σbc extending over all the wave-lengths for which b is tabulated. For some of these wave-lengths c is observed: let us distinguish these by adding a suffix o . For others values of c are obtained by interpolation among the observed c_o 's: distinguish these by the suffix e . Then

$$\Sigma bc = \Sigma b_o c_o + \Sigma b_e c_e.$$

But c_e is given a value that may be denoted by $\Sigma w_o c_o$, where w_o is the weight given in the interpolation formula to c_o in the evaluation of c_e . Thus on rearranging we have

$$\Sigma bc = \Sigma b_o' c_o,$$

where

$$b_o' = b_o + \Sigma b_e w_o.$$

The quantity b_o' is a typical entry of the new condensed table, and it is clear that the contribution to b_o' from the excluded entries b_e is the value of b derived by high order interpolation from the set b_e alone.

In constructing the tables which follow the interpolations were made by the Lagrangian formula of the 20th order. Preliminary investigation had shown that the application of a still higher order formula would not modify results given to the number of places retained in the standard tables. The accuracy of the final result is checked to some extent by the agreement of the new sums for the equal energy stimulus with the old. To check the results still further, and at the same time to provide other tables of value, the contracted table has been applied to the three standard illuminants of the C.I.E. system. In this calculation these illuminants have been regarded as specified by the alternate entries of the C.I.E. Table V*, which, apart from the extensions beyond $720\text{m}\mu$., agree with the particulars given in the earlier Table II†. After the products had been found and summed every entry was divided by the sum obtained for the y coordinates, exactly in the same way as was done in preparing Tables VI, VII and VIII‡ for the previous paper. The new

* *Trans. Opt. Soc.* 33, 102 (1931-32).

† *Ibid.* p. 77.

‡ *Ibid.* pp. 103, 104, 105.

totals after division and cutting down the number of figures compare with the old totals as shown in table 2:

Table 2

Source	x coordinate		z coordinate	
	Condensed	C.I.E.	Condensed	C.I.E.
Illuminant A	109·8450	109·8472	35·5824	35·5824
Illuminant B	99·0915	99·0930	85·3094	85·3125
Illuminant C	98·0699	98·0705	118·2216	118·2246

These results show that for smooth energy distributions such as these illuminants the coordinates derived from the condensed tables are indistinguishable from those given by the fundamental tables.

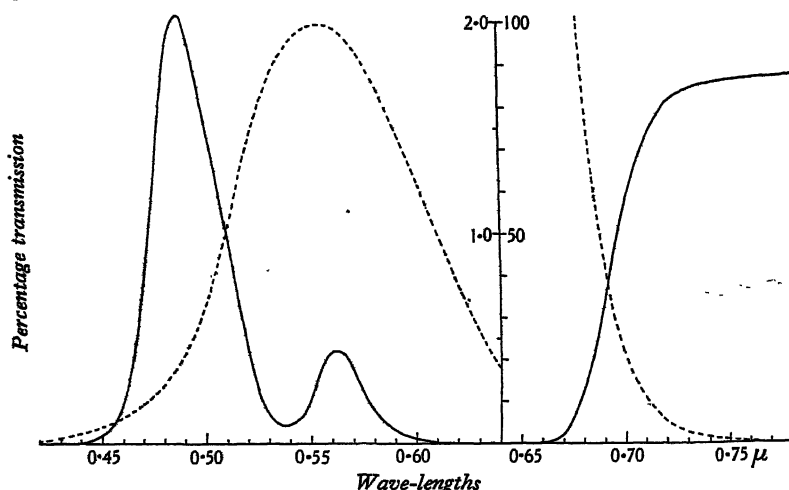


Figure 1. The full curve shows the transmission of a dichroic filter, the ordinate scale for the shorter wave-lengths being fifty times that for the longer wave-lengths. The broken curve represents the standard visibility function, the scale for the shorter wave-lengths being one-fiftieth of that for the longer wave-lengths, thus enabling the products of the ordinates of the two curves to be approximately visualized on a uniform scale for the whole spectrum.

As a further check a computation has been carried out with both tables on a dichroic filter which exemplifies a distribution that might be expected to indicate the presence of faults in certain parts of the new table if it did not indeed happen to illustrate conditions in which these tables could not be safely applied. The results, which are given in the accompanying tables, show that the new procedure agrees well with the old in this example also. The transmissive properties of the filter were measured by Mr H. G. W. Harding and are shown graphically in figure 1. It will be seen that the filter completely absorbs light of the shortest wave-lengths and also that of an intermediate range of wave-lengths. The transmission factors are very different in the two regions where light is passed, as is shown by the scale of ordinates being fifty times as great for one region as for the other. The dotted curve shows the standard visibility function, with the scales in the two parts altered in the inverse ratio to that for the transmission curves. The two taken in con-

junction enable us to see that there is not a great disparity in the light that would be transmitted in the two regions if a moderately high temperature source were used. The small hump in the neighbourhood of wave-length $560\text{m}\mu$. is of much importance, since it occurs where the visibility of light is greatest. The maximum transmission here is less than one-half of 1 per cent. In spite of this low value good accuracy is obtainable in the measurements with modern equipment. The advances that have been made as compared with pre-war spectrophotometry will be realized from the fact that observations on this part of the curve were made at every $5\text{m}\mu$. and that the curve has been drawn to pass exactly through every plotted point. On the other part of the curve observations were made at every $5\text{m}\mu$. up to $700\text{m}\mu$. and beyond that at every $10\text{m}\mu$. In the region where the transmission exceeds 80 per cent. two or three of the observed points lie just off the curve by an amount about equivalent to the thickness of the line in the drawing. Owing to the distribution and the values of the transmissions the colour of a source viewed through this filter changes rapidly with the colour temperature of the source. If the slopes of the transmission and visibility curves in the diagrams are considered it will be seen that this filter is likely to provide a good test for the new tables.

It is interesting to consider the contributions of the two regions of transmission separately. This can be done since the transmission factor falls to and remains at zero for a considerable length of the spectrum between the two regions. Taking first the band of shorter wave-lengths, the contributions to the x , y , and z sums were evaluated with the full tables using the measurements made at every $5\text{m}\mu$., and also with the condensed tables completely neglecting the observations at the odd wave-lengths. The leading figures in the values obtained are as follows:

Table 3

Source	x C.I.E.	x cond.	y C.I.E.	y cond.	z C.I.E.	z cond.
A	10884	10880	24329	24369	19416	19435
B	12966	12959	31614	31674	37978	38002
C	14027	14018	34710	34780	48087	48109

As the observations are recorded to three significant figures, this comparison is very satisfactory.

For the transmission band of longer wave-lengths the observations were partly at $5\text{m}\mu$. intervals and partly at $10\text{m}\mu$. intervals. The difference between the two totals was therefore computed by first finding the differences between the measured and the computed intermediate transmissions, the latter being based on the observations at the longer intervals only. The values obtained are as follows:

Table 4

Wave-length	Observed transmission	Computed transmission
655	0.00000	0.00023
665	0.00419	0.00422
675	0.064	0.05866
685	0.218	0.22464
695	0.471	0.46873

From the differences between the last two columns it is found that the differences made by the change to the new tables in this part of the spectrum are of the same small order of magnitude as with the shorter wave-length band.

The totals give the following comparative results:

Table 5

Source		<i>x</i> coordinate	<i>y</i> coordinate	<i>z</i> coordinate	Percentage transmission factor
A	C.I.E.	0.5117	0.3402	0.1480	0.4462
	Cond.	0.5113	0.3404	0.1483	0.4463
	Diff.	- 0.0004	+ 0.0002	+ 0.0002	+ 0.0001
B	C.I.E.	0.3453	0.3446	0.3101	0.4221
	Cond.	0.3448	0.3449	0.3103	0.4225
	Diff.	- 0.0005	+ 0.0003	+ 0.0002	+ 0.0004
C	C.I.E.	0.2862	0.3361	0.3776	0.4280
	Cond.	0.2858	0.3365	0.3777	0.4286
	Diff.	- 0.0005	+ 0.0004	+ 0.0001	+ 0.0005

It need hardly be said that the differences exhibited here are far below those which are perceptible to our eyes. It is instructive to compare them with the large differences of colour coordinates consequent on changing from one source to another. The transmission factor passes through a minimum value as the source increases in colour temperature. This might have been foreseen from an examination of the curves in figure 1. On the other hand the *y* coordinate passes through a maximum value.

While these examples show that the new tables may often be used with advantage in place of the full standard observer results, it must be emphasized that unlike the full tables they do not specify the standard observer, that they should only be used when it is certain that they will give results in agreement with the full tables, and that when the two differ only the results derived from the full tables have any recognized meaning. The responsibility for deciding when the new tables may properly be used, and labour thereby be saved, must rest in every case upon the experimentalist, who will be guided by the regularity or irregularity of the curve defined by his observations. There is much evidence available to show that the contracted tables may very often be used without sacrificing accuracy, but it is not at the moment possible from existing measurements to provide real typical illustrations of the conditions in which they may not be used. It is of course easy to construct theoretical energy distributions which are not adequately specified by their values at 10 m μ . intervals, and for these the new tables would certainly be unsuitable.

NOTE ADDED FEBRUARY 26, 1934

Since this paper was written Mr Harding has measured the transmission of a filter for isolating the green line from the mercury spectrum. This filter looks a pure yellow by transmitted light although it transmits no spectral yellow. The

observations taken at every 5 $m\mu$. are shown in figure 2, and the freehand continuous curve shows very approximately the transmission values based on these observations. Alternate observations are indicated by large and small dots, and the broken curve represents the transmission values that would be expected when the latter group of observations is disregarded. At the top of the diagram the general character of the errors made by neglecting these observations is shown. Owing to the somewhat irregular shape of the full curve and to the rapidity with which the transmission is changing at some parts of the spectrum these errors are very large in comparison

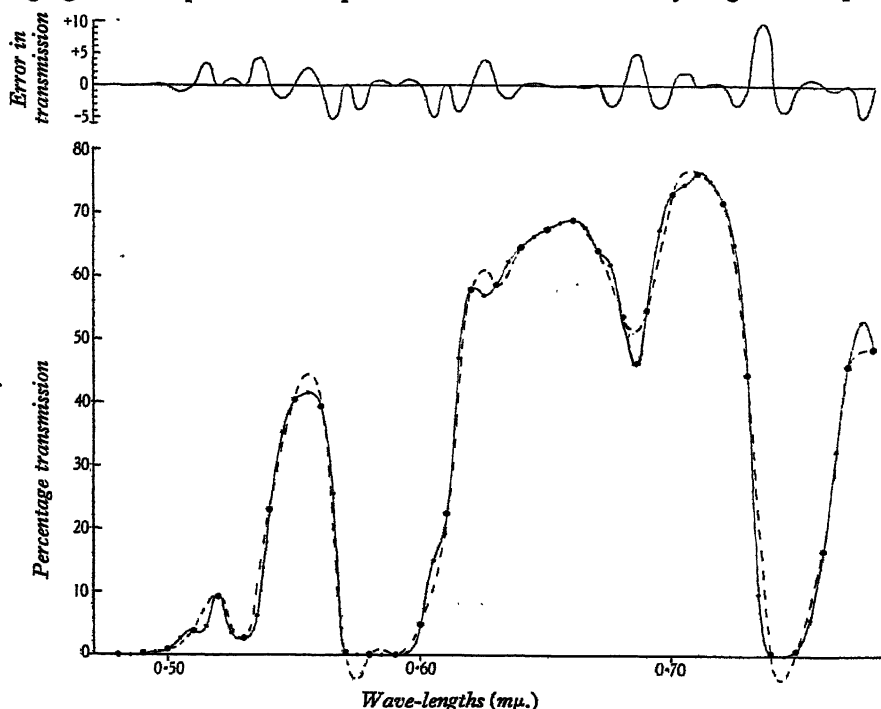


Figure 2. The full curve represents the measured transmission of the filter, and the dotted curve the transmission corresponding to alternate measurements only. The difference between the two curves is shown above. From inspection of this curve too high a value of y (excess of green) and too low a value of x (deficiency of red) is to be expected, and this is borne out by the calculations.

with any possible errors of measurement. With source *B* the C.I.E. colour co-ordinates corresponding to the full curve, and those obtained by using the condensed tables are as shown in table 6.

Table 6

	x co-ordinate	y co-ordinate	z co-ordinate	Percentage transmission factor
C.I.E.	0.5520	0.4426	0.0054	18.53
Condensed	0.5491	0.4451	0.0058	18.30
Difference	- 0.0029	+ 0.0025	+ 0.0004	- 0.23

The colour with any reasonably white source is a good yellow, the hue wavelength lying between 586 and 587 m μ . with a white constituent of approximately 1½ per cent. Mr Guild informs me that these differences between the C.I.E. and the condensed results, and also the departure from spectral purity, correspond to differences of colour that are measurable but not evident on inspection. As regards hue this is borne out by the recent investigation on hue-discrimination by Dr Wright and Mr Pitt, who in this region of the spectrum give 1 m μ . as their threshold difference. The relevant spectral colour coordinates of the C.I.E. standard observer are as shown in table 7.

Table 7

λ	x	y	z
586	0.5510	0.4482	0.0008
587	0.5572	0.4421	0.0007
Difference	+ 0.0062	- 0.0061	- 0.0001

In this particular case we may then say that the result given by the condensed tables would be quite satisfactory for ordinary commercial purposes, but not for standardization work.

From the character of the error curve given in figure 2 it is evident that the very fair agreement between the coordinates derived from the two sets of tables is due to the random distribution of the errors made by neglecting alternate observations. It is not of course permissible to assume that in any particular case gross errors such as those exhibited in figure 2 will tend to neutralize one another in the way or to the extent they happen to have done in this example.

DISCUSSION

Mr J. GUILD. I think everyone who has at any time to compute colorimetric quantities from energy-distribution data will find it helpful to have these condensed tables in a self-contained and convenient form. The tables being computed so that the sums of the various columns are the same as those of the corresponding columns of the official C.I.E. tables, we have the advantage that quantities evaluated by means of the condensed tables can be directly compared with corresponding quantities computed by means of the full tables without the trouble of reduction to a common denominator. This is particularly useful in the case of the tables for the standard illuminants, as ΣEyt (where t is the transmission or reflection factor of a specimen) gives directly the photometric transmission or the brightness factor of the specimen for the illuminant in question.

There is a statement in the paper which is liable to an interpretation which I am sure the author does not intend. This is the sentence, in the second paragraph, which begins: "The formally correct procedure when this is known...." In his preceding paper he has shown that there is no point in evaluating an integral by summing more terms than there are observed values of either factor in the integrand, whereas the sentence I have quoted may be read as contradicting this and implying

that there are circumstances in which the "formally correct" procedure is, in fact, to interpolate between the measured values. I hope the author will remove any possibility of misapprehension on this point by explaining more fully what he means to convey by "formally correct."

My own view is that if I obtain colour coordinates from energy-distribution data at 10-m μ . intervals, say at 400, 410, 420 m μ . etc., I am necessarily obtaining only an approximation to the correct C.I.E. values, and I cannot get (or rather cannot know that I get) a better degree of approximation than is obtained by simply adding the products, at these intervals, in accordance with the conclusion in the author's previous paper. If I were to displace my observation wave-lengths by 5 m μ ., so that they occur at 405, 415, 425 m μ . etc., I should, in general, get an appreciably different result from the summation of products, but this difference is unavoidable, being twice the error inherent in either of the separate attempts to obtain the result from incomplete data. I cannot see that there is any way of reducing this uncertainty, the only "formally correct" procedure for obtaining the correct result being in fact to determine the experimental factors at all the tabulated wave-lengths. When we depart from this procedure we do it deliberately, on grounds of economy, when we have reason to believe that the error in the result will not be as great as that which we are prepared to tolerate.

The surprising thing which is shown by the examples selected by the author is that these errors are so small even with absorption curves of extremely peaky and irregular character. The conclusion which I should form on this evidence is that colour-computation from experimental data at 10-m μ . intervals, carried out with these condensed tables, is amply accurate in 95 cases out of 100, but is not good enough, in some cases, for the present standard of accuracy in standardization work. There is, however, a considerable amount of repetition in such work, and the magnitude of the error can be determined by comparing the results obtained from a complete set of measurements with those deduced from a half-set (10-m μ . intervals) for one specimen of any given type. If the error is negligible for the purpose in view, work on all other specimens of the same type can be confined to the larger intervals.

Needless to say, the condensed tables will be of no use to those who imagine that the existence of "standard-observer" tables renders it practicable to evaluate colour coordinates from energy-distribution data to as many significant figures as there are available places on a computing machine. It is sometimes overlooked that the quantities of photometry and colorimetry are physical properties of things, and that *something* has to be measured before we can evaluate them. The best spectrophotometric technique places limits on the significant precision of a colorimetric result computed from energy-distribution, which is ludicrously low compared with that to which significance is attached in some colour calculations. If, however, we are prepared to regard colorimetry as a practical branch of metrology, and not as an arithmetical exercise, these condensed tables are quite accurate enough for a large proportion of the computational work which requires to be done.

Dr W. D. WRIGHT. The condensed tables should be welcomed by colorimetrists both for their own value and as an indication of the trend of opinion on the subject. In standardizing the colour-mixture data for a normal eye, the International Illumination Commission provided tables in which, so far as could be anticipated, interpolation would never be necessary. This meant, on the other hand, that the values were specified at more frequent wave-length intervals than would in general be required, so that the amount of work involved in spectrophotometric calculations appears unnecessarily formidable. The more this work can be reduced the better, and for this reason it would be interesting to know whether the author contemplates the preparation of tables with still larger wave-length intervals. In many cases it should not be necessary to take more than 20 points throughout the spectrum.

It would, I think, add to the value of the paper if the data on the second filter, discussed by the author in the reading of his paper, could be included. The results on the first filter, as given in table 5 on page 378, show that the errors introduced with the condensed tables were quite negligible, and they suggest that even fewer points could have been used. An absorption curve in which the errors become appreciable would therefore be of considerable interest. It would also be of interest to know whether the author has made any calculation of the differences between the values obtained by using the condensed tables and those taken from alternate entries in the original tables.

Finally, I gathered from the author's remarks that the tendency in some countries is to use enlarged, rather than condensed tables. This seems an unnecessary elaboration, and one that would not be favoured by the industrial worker. It would be interesting to know whether this trend originates in the industry itself or in the National Laboratories.

AUTHOR'S reply. By the formally correct procedure in calculating colour coordinates on the C.I.E. system I mean computation using the full Standard Observer tables with transmission values for the filter considered (or equivalent data for other materials) for intervals of $5\text{ m}\mu$. If it is known, as I have specifically laid down in the passage referred to, that we get accurate results for the properties of the material at the $5\text{ m}\mu$. intervals by interpolating from observations at twice this interval, we naturally interpolate instead of measure, and then proceed as though we had measured everywhere. This is the procedure which I think would have been adopted by everyone at the time the C.I.E. colorimetric system was established, and for the reason that it was the course then contemplated I refer to it as the formally correct procedure.

The preceding paper to which Mr Guild refers shows that we can get the same result under these circumstances with less labour. The condensed tables of this paper are those by which this result can be reached. The alternate entries of the full Standard Observer tables do not yield this result, though they nearly always give a very good approximation to it. Under the conditions we are assuming, the full Standard Observer and the condensed tables give the same result, any differ-

ences in the final figures being due wholly to the limitation in the number of figures retained in each entry of the condensed tables, and these are necessarily of trivial magnitude. I should not under those conditions therefore consider the figures given by the condensed tables as an approximation to the correct result, but as the correct result itself. What was the formally correct procedure is therefore no longer the one which ought to be followed. As soon however as we do not know that observations at $5\text{ m}\mu$. intervals will agree with interpolations from measurements at $10\text{ m}\mu$. intervals the position alters. If measurement at these intervals is all that is available the best result is likely to follow from the use of the condensed tables, but this result will in general be found somewhat in error if observations at every $5\text{ m}\mu$. are subsequently taken and the full C.I.E. tables are used. The examples however suggest that this error will usually be quite small. In any event it is attributable solely to the inadequacy of the spectrophotometric work.

In reply to Dr Wright I have added to the paper particulars of the second filter. I have already pointed out that it is better to use the condensed tables* than alternate entries of the full tables. The differences resulting from using the two alternate sets of entries are known for many coloured materials and are in general quite small. They provided the evidence that tables with larger intervals could often be used without introducing a sensible error. Before preparing the paper I considered still more contracted tables, but the results of partial computation led me to think that they would not prove very useful. An interval of $20\text{ m}\mu$. is certainly too wide to be acceptable for any of the regular work carried out at the National Physical Laboratory, and I should hardly expect to find that anyone would adopt so large an interval after giving it a fair trial over a wide range of colours. It is not unimportant to remember that as the intervals are further increased the saving of labour becomes much less appreciable, while the possible errors increase very rapidly. With a reduction to 20 observations for the whole visible spectrum the additional labour-saving is only 25 per cent, while the outstanding errors are likely in general to be something like five times as great, and in particular cases they may easily be increased ten times or more.

Like Dr Wright I have been puzzled by the elaboration of the C.I.E. tables which has been carried out elsewhere. I have not heard how this movement originated and I do not understand its purpose.

* It would of course be possible to make almost trivial alterations in the Standard Observer tables which would enable alternate entries to be used instead of special tables, but it seems undesirable to alter these agreed figures.

AN APPARATUS FOR THE OPTICAL PROJECTION OF THERMIONIC VALVE CHARACTERISTICS

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ABSTRACT. A simple and robust apparatus has been developed, primarily for lecture demonstrations, to show the various characteristic curves of thermionic valves on a screen of any desired size. Two mirror oscillographs are employed with axes at right angles, one indicating anode current and the other the grid potential. A suitable alternating voltage of small amplitude from a 50-cycle supply is applied to the grid, causing the characteristic to be traced out 50 times a second, and persistence of vision causes the whole curve to be visible. The instrument indicating current is a Sprenger oscillograph, while the voltage-controlled vibrator is a special instrument designed for the purpose and described in the paper.

§ 1. INTRODUCTION

THE present apparatus has been developed for the purpose of showing to a large audience the (grid-volts, anode-current) or mutual characteristics, and (anode-volts, anode-current) or anode characteristics, and to demonstrate the effect of the variation of the internal and external conditions. In addition to the usual static characteristics, the dynamic characteristics (taken with load in the anode circuit) can also be studied. In this way the difficulties in the accurate matching of reactive loads can be shown.

A mechanical apparatus of this kind possesses advantages in cost, simplicity, and portability over a cathode-ray tube.

§ 2. MODE OF OPERATION

A beam of light from a gas-filled lamp, pointolite, or arc lamp, according to the size of picture required, is reflected successively by two mirrors which vibrate about horizontal and vertical axes respectively. The first mirror is deflected by a current-controlled oscillograph mechanism connected in the anode circuit of the valve, and its angular displacement at any moment is proportional to the anode current at that moment. After reflection from the current-controlled vibrator, the beam strikes a second mirror attached to the voltage-controlled vibrator and rotating in synchronism with the grid or anode potential as desired. The spot of light on the screen takes up a position on the characteristic curve of the valve, and the whole curve is traced out if the potential is varied continuously. It is convenient to use the

standard 50-cycle supply for this purpose, and a perfectly steady trace without flicker is thus obtained.

Owing to the fact that the beam of light reflected from the first mirror moves through an appreciable angle, the second mirror must have a length of about $1\frac{1}{2}$ in. in a direction parallel to its axis of rotation. No suitable oscillograph could be found to satisfy this condition, and a special indicator, described below, has been designed for this purpose.

If an opaque screen is used, lines can be drawn upon it to represent the axes of the curves. If, however, a ground-glass screen is used, the trace being projected from the side remote from the observers, it is desirable to show the axes as bright lines. The beam of light should then be made slightly broader, so that part is reflected from fixed mirrors alongside the moving ones. The Sprenger oscillograph used as the current-indicating vibrator is already fitted with such a mirror, and one can easily be fitted to the voltage instrument. By this means two perpendicular bright lines are shown on the screen. Their positions can be adjusted to the current and voltage zeros by switching off the vibrators, and turning the appropriate fixed mirrors so as to bring the axis spots into coincidence with the curve spot.

§ 3. THE CURRENT-CONTROLLED VIBRATOR

Any magnetically-operated oscillograph of sufficient sensitivity can be used here, provided that it will operate with its axis of rotation horizontal, but the choice is very much limited by these two conditions as to sensitivity and plane of operation. Sufficient deflection should be produced by a current of a few milli-

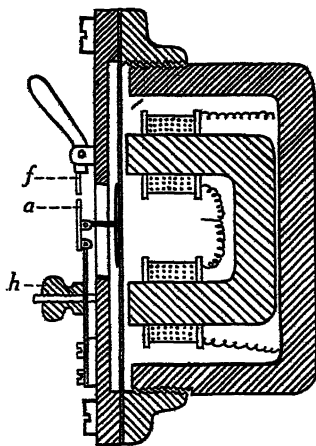


Figure 1. The Sprenger oscillograph. *a*, vibrating mirror; *f*, fixed mirror; *h*, zero-adjustment.

ampères, and a variable shunt should be provided to make it suitable for use with different types of valves.

If the object in view is simply to demonstrate the behaviour of valves in a general manner, and not to examine any particular type of valve, it is possible to obtain

a valve of one of the types giving an anode current of 50 or 100 mA., and this, of course, imposes less severe restrictions on the design of the oscillograph. If, however, the apparatus is required to work with a valve passing only 5 mA. or so, then the only suitable oscillograph known to the author is the Sprenger.

The Sprenger oscillograph, shown diagrammatically in figure 1, is similar to a rather large telephone movement having a resistance of 3000 Ω . Attached to the centre of the diaphragm is a small circular mirror *a* pivoted so that movement of the diaphragm causes the mirror to rotate on its axis. A variable amount of frictional damping can be applied to the mirror, and its equilibrium position is also adjustable by means of a thumb screw *h*. The instrument is usually supplied complete with a small gas-filled lamp of the motor-headlight type, pin-hole screen, and lens. The whole of this optical system is mounted on a frame with the oscillograph instrument and it remains permanently in correct alignment with it. For work with a small opaque screen, or a moderately large translucent ground-glass screen with projection from the rear, the optical system can be used without alteration. When extra brilliancy is required it will be necessary to use a pointolite or arc lamp with suitable optical arrangements to obtain an intense beam.

§ 4. THE VOLTAGE-CONTROLLED VIBRATOR

The usual types of oscillograph have, of course, small light mirrors so that they can readily follow the rapid variations of current without considerable expenditure of power. But for the present purpose a long mirror is necessary in order that the spot of light after deflection at the current oscillograph may not move right off the second mirror. However, a low frequency such as 50 c./sec. may be used, and the

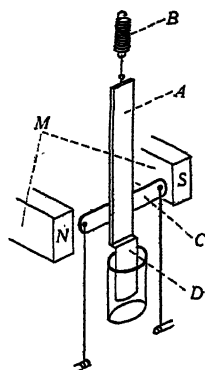


Figure 2. Moving system of voltage-controlled vibrator.

power available can be practically unlimited, so that there is no difficulty in using a mirror $1\frac{1}{2}$ in. long. A moving-iron type of instrument has been constructed. For the present arrangement the moving-iron pattern has obvious advantages in simplicity over the moving-coil pattern. The moving system, shown in figure 2, consists of a strip of glass mirror *A*, $\frac{1}{4}$ in. wide and $1\frac{1}{2}$ in. long, suspended by a small wire hook from a spiral spring *B*. Cemented to the back of the mirror, near its

lower end, is a strip of stalloy *C*. Two linen threads, of the kind used for sewing, are attached to the outer ends of the strip and pass downwards to adjustable supports. An aluminium damping vane *D*, also cemented to the back of the mirror, dips into a glass tube containing oil. The depth of immersion can be altered by raising or lowering the oil-chamber. The arrangement is thus practically an inverted bifilar suspension. The natural frequency is made high by the application of considerable tension to the spring *B* through the screw and nut. The screw is slotted to prevent it from turning when the nut is rotated.

The stalloy strip is suspended between the poles of a large horseshoe permanent magnet *M* which also tends to keep the moving system in its equilibrium position. The deflecting force is provided by the coil *F* which produces a magnetic field perpendicular to the field produced by the permanent magnet. The strip of stalloy *C* accordingly takes up its position along the resultant magnetic field due to the two perpendicular components. Any desired degree of damping can be obtained by using oil of suitable viscosity, and the depth of immersion of the vane is also variable. The coil can be wound so as to be suitable for direct connexion across the potential-difference applied to the grid or anode circuit, but it is preferable to wind a coil of comparatively few turns, and to use an external series resistance or potential-divider to obtain a suitable amplitude of vibration. In this way a wide range of conditions can be accommodated according to the type of valve, size of screen, etc.

§ 5. (GRID-VOLTS, ANODE-CURRENT) CHARACTERISTICS

The circuit and arrangement of the vibrators is shown diagrammatically in figure 3. The potential of the grid is varied periodically by the application of an

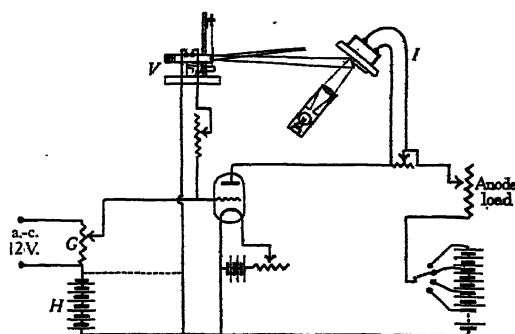


Figure 3. Circuit for (grid-volts, anode-current) curves.

a-c. supply of about 20 peak volts, adjustable by means of the potential-divider *G*. The battery *H* enables the grid-swing to be varied from 0 to -40 V. instead of from $+20$ to -20 V., should it be undesirable to show the characteristic to the right of the zero-grid-volts line. The grid potential at any instant is indicated by *V*, the specially constructed instrument, while the corresponding anode current is shown by *I*, the Sprenger oscillograph. Since the steady component of the potential-difference only displaces the mirror of *V* permanently to one side, it is often

possible to transfer the connexion of the vibrator to the upper, positive end of the battery as shown in the dotted connexion. The battery is then not called upon to supply any current, and can be of the usual dry-cell type.

The effect of variation of the filament temperature on the saturation current is at once apparent, and by increasing the anode voltage, the shift of the curve bodily to the left is readily shown.

§ 6. (ANODE-VOLTS, ANODE-CURRENT) CHARACTERISTICS

The Sprenger oscillograph is connected in the anode circuit, whilst the voltage-controlled vibrator in series with an adjustable resistance, is connected across the anode supply, the potential of which is made to vary periodically from 0 to, say, 300 V. by combining a steady potential with an alternating potential having a peak value equal to the steady potential. The connexions are shown diagrammatically in figure 4.

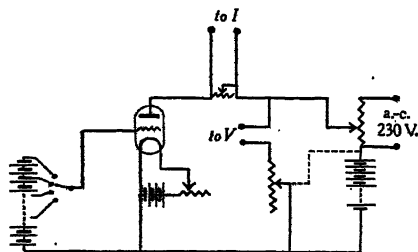


Figure 4. Circuit for (anode-volts, anode-current) curves.

For accurate results the voltage-controlled vibrator should be connected across the combined a.-c. and d.-c. supplies, but as this involves an appreciable strain on the battery supplying the d.-c., it is often better to connect according to the dotted line, across the a.-c. supply only, and to rotate the instrument bodily to give the effect of the steady d.-c. deflection.

If the grid potential is adjusted to various negative values the usual family of curves will be shown, enabling suitable operating points to be found for the valve when used as an amplifier. It is desirable that the grid potential should be changed in steps rather than continuously, so that tapings from the battery should be taken to a rotary switch. The usual precautions are necessary to avoid short-circuiting the intermediate sections of the battery when changing from one tap to the next.

The effects of secondary emission of electrons from the anode can be shown if the grid is maintained at a positive potential rather greater than that of the anode. The negative-resistance properties of the dynatron are shown in this way.

It may be mentioned that by replacing the valve by a fixed impedance the effect of combining two oscillations in perpendicular planes and having various phase relationships can be demonstrated. The well-known straight line, ellipse and circle are produced by altering the relative phases of the currents in the two vibrators.

For demonstration purposes, and perhaps also for routine testing of valves, absolute values of the quantities shown in the curves are not required, but if

necessary the scales can be calibrated. It is seldom, however, that a characteristic has to be determined to a high degree of accuracy.

§ 7. COMPENSATION FOR DISTORTION DUE TO INDUCTANCE OF OSCILLOGRAPH COILS

Owing to the inductances of the windings of the two indicators, there may be a slight phase displacement between the current and voltage, visible on the screen as a double track, and caused by the descending spot not following quite the same path as on its upward movement. This phase displacement may be corrected electrically by introducing capacity into the circuit, generally the anode circuit, in which the current is lagging. The voltage vibrator is made practically non-inductive by the use of a large series resistance.

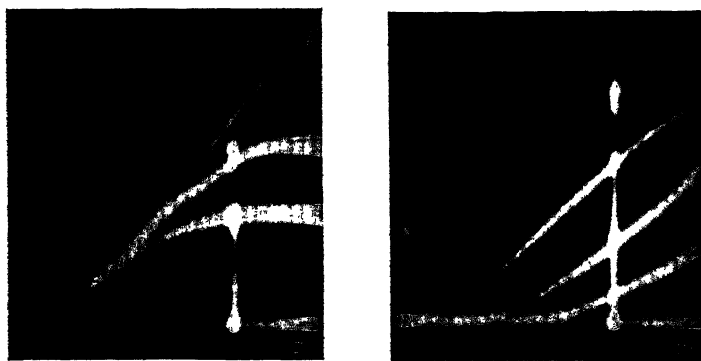


Figure 5. Examples of curves shown by the apparatus. (a) (Grid-volts, anode-current) curve with different filament brilliancies, showing effect on saturation current. (b) (Grid-volts, anode-current) curve at constant filament voltage and different anode potentials.

When the lag in the anode circuit is only slight, it is simpler to make the adjustment mechanically, by altering slightly the natural frequency of the vibrating system of the voltage-controlled vibrator. This is easily done by turning the milled nut at the top to alter the tension.

The phase relationship between the displacement and the deflecting force in a system vibrating under the influence of a periodic disturbance depends on the frequency of the applied force and the natural frequency of the system. If the latter is altered so as to pass through the resonant frequency, a large phase change occurs. In the present case the natural frequency will be kept well above the applied frequency, but a slight movement in this direction will serve to compensate for the lagging of the current in the anode circuit due to the inductance of the Sprenger oscillograph not being quite negligible.

§ 8. ACKNOWLEDGMENT

The author is indebted to Mr Hellary of the Imperial College workshops for the construction of the vibrator and for suggestions regarding the design of the adjusting devices.

DISCUSSION

Dr D. OWEN. The author's work represents a return to the mechanical type of curve-tracer, somewhat surprising in view of recent improvements in and reduction of cost of the cathode-ray oscillograph. It has the advantages, for some purposes, of producing oscillograms on a larger scale and with white light, and these may justify its use. It is important, however, to be assured of reasonably faithful reproduction, and the supply of data in regard to natural frequency and damping, is desirable both in regard to the Sprenger oscillograph and that of the author's own design.

Mr J. GUILD suggested that the need for a long second mirror, referred to at the top of page 385, could be obviated by the use of a fixed lens so situated as to produce an image of the first mirror on the surface of the second.

AUTHOR'S reply. In reply to Dr Owen: The apparatus, in the form described in the paper, is intended for lecture demonstrations. For such purposes an error of even 20 per cent would probably not be very important, the general shape of the curve being all that is required. Actually, however, the fact that the ascending and descending traces coincide within close limits indicates that the curve is faithfully reproduced to approximately 2 per cent. The natural frequency of the Sprenger oscillograph is about 800 c./sec. and the damping is adjustable. The frequency of the voltage-indicating instrument as arranged for operation is approximately 200. This can easily be made much higher, but at that setting compensation is obtained for the lag of the anode current due to the inductance of the anode-current oscillograph. Critical damping can be applied by means of the adjustable oil chamber. In spite of the recent improvements in cathode-ray tubes, it still is not possible to obtain curves of the size and brilliance given, at a small fraction of the cost, by this apparatus without any subsidiary gear.

In reply to Mr Guild: A lens system of the type suggested was given a preliminary trial, but discarded owing to an apparent loss of light. In view of his suggestion it is intended to make another test with more suitable lenses.

A SIMPLE METHOD OF DEMONSTRATING THE PARAMAGNETISM AND DIAMAGNETISM OF SUBSTANCES IN MAGNETIC FIELDS OF LOW INTENSITY

BY PROF. A. O. RANKINE

Received February 16, 1934. Read March 2, 1934.

ABSTRACT. The instrument described is the result of an attempt to construct a magnetic gradiometer capable of measuring small distortions of the earth's magnetic field in the same way as the Eötvös torsion balance measures non-uniformities of gravity. Although this purpose has not yet been achieved the first model of the instrument has revealed itself as a means of demonstrating in a convincing manner the paramagnetism or diamagnetism of substances of small susceptibility, for example, the diamagnetism of a few cubic centimetres of water. Moreover, the magnetizing fields employed are much smaller than has hitherto been customary, being of the order of 50 gauss or less. This first model of the instrument is imperfect in certain respects, mainly on account of the use of some brass in the construction. The objections to this material, on account of its ferromagnetic content, were not at first realized, and it will be necessary to construct a new apparatus, employing carefully chosen materials, before full advantage can be taken of the sensitivity available, and demonstration refined to precise measurement.

It seems certain that gases also may be brought within the scope of accurate determination, particularly if access can be had to a suitable laboratory. The present apparatus, however, behaves well enough to warrant description, which is made pending the projected modifications.

The system used also provides a basis for the construction of a new form of very sensitive galvanometer, and this matter is discussed briefly.

§ 1. INTRODUCTION

IN 1896 Eötvös* described a magnetic torsion balance which he had constructed for the purpose of measuring spatial non-uniformities of the earth's magnetic field in a way analogous to the operation of his gravity torsion balance. The two instruments are, indeed, described in the same paper. It appears, however, that whereas the gravity balance has since become very widely used in geophysical surveying, the magnetic instrument has produced no important results, if, indeed, it was ever used in the field. The present author began some two years ago to investigate the possibilities of a modification of the Eötvös form of magnetic torsion balance, and mentioned the principal practical difficulty in his presidential address to Section A of the British Association in 1932. It soon became clear that this difficulty, although it prevented the realization of a field magnetic instrument in

* *Ann. d. Phys.* 59, 375 (1896).

all respects analogous to the gravity balance, did not operate in any substantial manner against the use of the Eötvös principle in a laboratory instrument for measuring magnetic field distortion deliberately caused in the proximity of the apparatus. The result has been the construction of an instrument of an exceptionally sensitive character by which the magnetization of, for example, water in comparatively weak fields of the order of 50 gauss can be readily demonstrated.

The system proves to be virtually that which Kapitza and Webster* rejected as "practically impossible" on account of the smallness of the forces involved. Instead, it is now found to be almost absurdly easy to operate. The surprising thing is that until now no one seems to have realized the magnitude of the force between the pole of a small permanent magnet and a piece of feebly susceptible material really close to the pole, in relation to the delicacy of torsional suspensions about a vertical axis, as opposed to the horizontal axis employed by Kapitza and Webster*.

In the first model of the apparatus now to be described there have been incorporated those suspensions and materials which came readily to hand. The use of ordinary brass in certain constructional elements has proved to be objectionable on account of the ferromagnetic content. As a result, and in a way which is itself of considerable interest, the sensitivity of the instrument is actually reduced to about one-ninth of its nominal value. In spite of the uncertainty as regards precise measurement thus introduced, the system behaves remarkably well, and makes it easy to demonstrate the magnetization in weak fields of slightly susceptible substances. For example, a test-tube of distilled water placed suitably in the apparatus shows a repulsion between it and a magnet pole of about 50 c.g.s. units by a deflection of 5 or 6 cm. of a spot of light on a scale 2 m. distant. Moreover, the balance displays just that immunity from response to large scale temporal fluctuations of the earth's magnetic field (such as diurnal variations and even magnetic storms) which one would anticipate from the theory underlying its operation. Even those erratic fluctuations of artificial origin (usually attributed to the electric currents of railways and trams) which are often so troublesome in magnetic measurements in London laboratories are here ineffective. Only magnetic disturbances of relatively local origin, such as those due to movements of ferromagnetic material in neighbouring rooms, produce any appreciable variation of zero, which is otherwise remarkably constant. It does appear, however, that in order to take full advantage of the sensitivity available, the work must be done in a laboratory in which there can be strict control of any iron or any electric currents. Under these conditions, and with the apparatus reconstructed employing the most suitable materials, calculation provides no reason for doubting that the susceptibilities of gases, even at reduced pressures and in fields of only a few gauss, can be measured with satisfactory precision. As the present apparatus demonstrates the possibilities in a sufficiently striking manner it is considered appropriate to describe its nature and behaviour now, pending the projected modifications of construction and procedure.

* *Proc. R.S. A* 132, 443 (1931).

§ 2. PRINCIPLE OF THE APPARATUS

Consider a system consisting of a horizontal beam (AB , figure 1) of non-ferromagnetic material suspended by a torsional wire or strip CO from a point C vertically above its centre of gravity. From the end A of the beam is suspended, by means of a fibre, a permanent magnet DE with its magnetic axis nearly vertical. (This axis can in fact never be quite vertical, except at the earth's magnetic poles, because the horizontal component of the terrestrial field causes it to tilt slightly.) From the end B of the beam a counterpoise FG of non-ferromagnetic material is suspended in a symmetrical manner, or it may be actually fixed to the beam in a suitable position. The poles of the magnet are approximately at N and S . Let τ be the torsional coefficient of the suspension CO and τ' that of the suspension AD ; and let m be the pole strength of the magnet.

First consider the equilibrium of the system in a spatially uniform magnetic field. The poles of the magnet being precisely equal and opposite in strength, the field gives rise to no translational force on the magnet—only couples. Consequently the remaining forces, of which there are only two—the weight of the magnet and the tension in the fibre AD —constitute a couple. Hence this tension is equal and opposite to the weight, i.e. it is *strictly vertical*. There is therefore no horizontal force on the end A of the beam. This is the essence of the argument. In a uniform magnetic field the system of horizontal forces on the beam consists of two couples only—those due to the twists in the central suspension CO and the subsidiary suspension AD respectively. The existence of these torsions arises from the fact that the magnet has always (except at the earth's magnetic poles) a horizontal component of moment which tends to make the magnetic axis lie always in the magnetic meridian. The control which the earth thus exercises is large compared with the torsional coefficients of suspending fibres of the necessary supporting strength. Accordingly the magnetic axis is always very nearly in the meridian, whatever azimuth the instrument may have, and the torsion in the fibres thus distributes itself between the central and subsidiary suspensions in the proportion $\tau' : \tau$. Thus if τ' is much less than τ , as it may readily be, the effect of the earth's horizontal field on the azimuth of the beam can be made relatively small. It is this effect, however, that prevents the full realization of the magnetic analogue of the gravity gradiometer*, but it is relatively unimportant from our present standpoint. We have generally, in fact, to work from a false zero with some torsion in both suspensions even in a uniform magnetic field. But a uniform field, however strong or inclined to the vertical, can do no more than decrease somewhat the sensitivity of the arrangement as determined by the torsional coefficient of the central suspension alone. The author has shown† that the effective torsional coefficient, i.e. the ratio between any horizontal force-moment applied externally

* The author has discussed this question in detail in his presidential address to the Physical Society, *Proc. Phys. Soc.* 46, 1 (1934).

† *Loc. cit.*

to the beam and the angle through which it turns in consequence, has a maximum value of $\tau + \tau'$. If only τ' , already small, could be reduced to zero the effective torsional coefficient would be simply that of the central suspension itself.

Now suppose that the field is made no longer uniform by the introduction, for example, of a piece of magnetizable material P near the pole S either in front of or behind the plane of the diagram in figure 1 (or the position indicated in almost end-on view in figure 2). This gives rise to a horizontal force of attraction or repulsion perpendicular to the vertical plane containing the beam. This force, acting mutually on the magnet pole and the specimen, causes the suspension AD to be no longer vertical, and the horizontal force is thus transferred to A , and

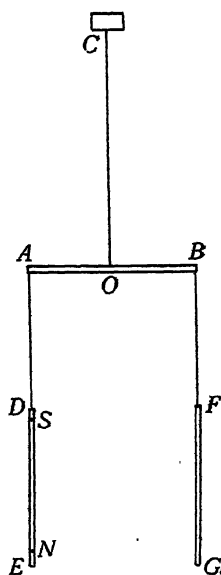
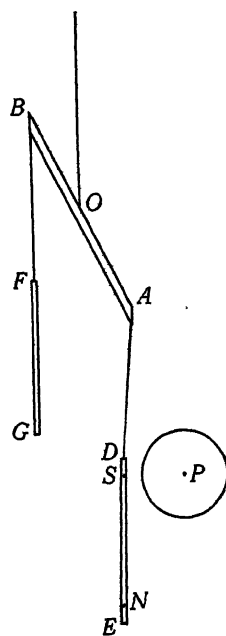


Figure 1.

Figure 2. Radius of sphere $P=a$; Distance $PS=c$.

results in a deflection of the beam until balanced by the torsion. Thus if F is the translational force applied to the magnet and θ is the resulting change of azimuth of the beam, the length AO being b ,

$$\theta = \frac{Fb}{\tau + \tau'}.$$

The question to be answered is whether the possible values of F , due to the magnetization of the specimen by the magnet pole, and in relation to the torsional coefficients, make it feasible with appropriate optical magnification to measure θ .

§3. MAGNITUDE OF THE FORCES OPERATING

Before describing the details of the apparatus it will be convenient to obtain approximate values of the forces of magnetic attraction or repulsion at our disposal. For this purpose we can regard the magnet pole S as situated at a point, and take as our specimen of material a sphere of radius a with its centre at a distance c from the pole (figure 2). It happens that the exact solution of this problem is available, from analogy with the corresponding case in electrostatics. Jeans* gives the formula for the mechanical force between a point charge e and a dielectric sphere as

$$F = \frac{1}{2} \beta e^2 \frac{a^3}{c^3} \left[\frac{1 + \beta}{c^2 - a^2} + \frac{2c^2}{(c^2 - a^2)^2} - \frac{c}{a^3} (1 - \beta^2) \left(\frac{a}{c} \right)^\beta \int_0^{\frac{a}{c}} \frac{x^{2-\beta} \cdot dx}{1 - x^2} \right],$$

where $\beta = \frac{K - 1}{K + 1}$, K being the dielectric constant.

The magnetic equivalent of e is m , the pole strength, and K corresponds to μ , the magnetic permeability. Thus we substitute for β the value

$$\frac{\mu - 1}{\mu + 1} = \frac{4\pi\kappa}{2 + 4\pi\kappa} = \frac{2\pi\kappa}{1 + 2\pi\kappa},$$

where κ is the magnetic susceptibility.

If we concern ourselves with values of κ small compared with unity, i.e. if we deal simply with paramagnetic and diamagnetic substances, the formula becomes simplified and the integration contained in it is performable. The author is unaware of this adaptation of the formula having been given previously and accordingly presents it.

With κ small as indicated, β becomes $2\pi\kappa$, and, being thus itself small, can be neglected in the formula except as the multiplier of the whole expression. We obtain

$$F = \pi\kappa m^2 \frac{a^3}{c^3} \left[\frac{1}{c^2 - a^2} + \frac{2c^2}{(c^2 - a^2)^2} - \frac{c}{a^3} \int_0^{\frac{a}{c}} \frac{x^2 dx}{1 - x^2} \right].$$

Writing $a/c = s$ (which < 1 necessarily) integration gives

$$F = \frac{\pi\kappa m^2}{c^2} \left[\frac{s(1 + s^2)}{(1 - s^2)^2} - \frac{1}{2} \log \frac{1 + s}{1 - s} \right].$$

This is conveniently transformed by the substitution $\log \frac{1 + s}{1 - s} = y$, which corresponds to $s = a/c = \tanh \frac{1}{2}y$.

The formula then reduces to

$$F = \frac{\pi\kappa m^2}{4c^2} (\sinh 2y - 2y).$$

For convenience of calculation of F the values of the function in brackets have been given in table 1.

For intermediate values of $\sinh 2y - 2y$ in relation to a/c a continuous curve can, of course, be drawn.

We may take, for example, a case which will be involved later, and assign the

* J. H. Jeans, *Electricity and Magnetism*, 1920 edition, p. 290.

Table 1.

y	$\frac{a}{c} = s = \tanh \frac{y}{2}$	$\sinh 2y - 2y$
0	0	0
0.2	0.0997	0.011
0.4	0.1974	0.088
0.5	0.2449	0.175
0.6	0.2913	0.309
0.8	0.3800	0.776
1.0	0.4621	1.627
1.2	0.5370	3.066
1.4	0.6044	5.392
1.6	0.6641	9.046
1.8	0.7163	14.686
2.0	0.7616	23.290
2.4	0.8336	55.951
3.0	0.9052	195.713

following values: $c = 1.80$ cm., $a = 1.28$ cm. and $m = 50$ c.g.s. units. The corresponding value of a/c is 0.711, and $\sinh 2y - 2y$ equals 14 approximately. Thus

$$F = \frac{\pi \times 2500 \times 14}{4 \times 1.8^2} \cdot \kappa = 8.48 \times 10^3 \kappa.$$

The maximum value of the field stimulating the material of the sphere is $50/0.52^2 = 180$ gauss approximately, and it falls off rapidly towards the remote side of the sphere. Assuming that κ has in such relatively weak fields the same value as that measured in fields of some thousands of gauss—an assumption needing verification and one which the present system promises to elucidate—we may anticipate that for water F will have the value $-7 \times 8.48 \times 10^{-4}$ dyne, or will constitute a repulsion of 5.9×10^{-3} dyne approximately. For air, taking $\kappa = 3.2 \times 10^{-8}$, the corresponding force, this time an attraction, will be 2.7×10^{-4} dyne. The detection of such apparently small forces is quite easy, as will be seen, if we take advantage of the delicacy of available torsional fibres suspended vertically.

§4. DESCRIPTION OF THE INSTRUMENT

In the instrument first made and now to be described full advantage has not been taken of the sensitivity actually attainable. The components have been chosen on the basis of immediate availability and can certainly be improved greatly, given the necessary time. The main suspension (a , figure 3), for example, is the metal strip which was previously incorporated in one of the gravity gradiometers used by the Imperial Geophysical Experimental Survey for gravity work in Australia during 1929–30. Its length is about 30 cm. and its torsional coefficient approximately 0.16 dyne-cm. per radian. It is much stouter than it need be for present purposes, as it would normally be used to support 100 gm. or more, whereas the

silk fibres are about 17 cm. long and have torsional coefficients of about 0.01 dyne-cm. per radian, which is small compared with that of the central suspension. They carry at their lower ends small hollow cylinders of brass into which are inserted the magnet and the counterpoise, friction giving adequate support. The magnet is of Darwin's 15 per cent cobalt steel $\frac{1}{8}$ in. in diameter and 5 in. long, and its magnetic moment of about 570 c.g.s. units has remained remarkably constant during the two years it has been in the author's possession. Its pole strength is estimated to be roughly 50 c.g.s. units. The counterpoise is a brass rod also $\frac{1}{8}$ in. in diameter, and, like the magnet, weighs approximately 8 gm.

In order to protect the suspended system against draughts and other air convection currents the whole is enclosed by a sliding vertical brass cylinder h , provided with a glass window j suitably placed to allow optical observation. The base, fitted with brass levelling screws is also of brass, and the upper part of the enclosure, including the brass tube k surrounding the central suspension and brass torsion head, is supported upon the base by three vertical pillars p_1 , p_2 and p_3 at 120° apart as shown in figure 4. These are of $\frac{1}{4}$ -in. brass rod, and play an interesting part in the behaviour of the apparatus, as will be seen later.

To allow specimens of various substances to be brought into the necessary close proximity to the magnet poles two metal tubes l , closed at the bottom and open at the top, project vertically into the interior of the case. Into these the specimens can be lowered. One could, of course, employ the forces due to *both* poles, since the force depends upon m^2 . I have preferred, however, to use the lower pole N to secure electromagnetic damping by causing it to move in the annular space between two copper cylinders (g) $\frac{1}{8}$ in. thick. It is easy to adjust the positions of the cylinders so that the suspended system is critically damped. Accordingly the closed bottoms of the tubes l reach only a few centimetres below the upper magnet pole S , and the effect on only one pole is used for purposes of deflection. The tubes themselves were originally of brass of internal diameter 2.8 cm., and of thickness 26 s.w.g.; their axes were about 3.7 cm. apart, so that the axis of the suspended magnet in the symmetrical position was about 4 mm. from the outer surface of each cylinder. These surfaces served the purpose of stops, limiting the angular amplitude of the suspended system to between 5 and 6 degrees. It was quickly discovered, however, that these brass tubes exercised a large magnetic control, presumably on account of their content of iron. The magnet, on approaching either tube, gathered speed and eventually remained in contact with the tube, unless it rebounded and stuck to the opposite tube instead. The substitution of specially made copper tubes of nearly the same dimensions surmounted this difficulty, and a stable zero was secured.

The vertical brass pillar p_1 produced an unexpected effect, greatly diminishing the sensitivity of the arrangement. It was observed that if a second brass rod (like the counterpoise) was substituted for the magnet, the period of oscillation of the system about the central axis was about 165 sec. This became reduced to about 55 sec. with the magnet in place. A considerable control, additional to that of the central suspension, was implied, the total control being nine times that of the sus-

pension, since the periods observed are in the proportion 3 : 1. This extra control was traced to the attraction between the brass pillar p_1 and the magnet, affecting in this case both poles. In the symmetrical position the pillar is about 1 in. from the magnet, yet in a deflected position a component of the attraction, even at this distance, provides a substantial restoring force. This action was verified by later observations in which it appeared that the beam had two other positions of stability, namely, when the vertical plane through it passed nearly through one or other of the remaining pillars p_2 and p_3 , even though 120° of torsion existed in the suspension.

The brass pillars still remain in the instrument as it serves purposes of demonstration well, and, indeed, it is not considered worth while to secure the additional sensitivity clearly available (in the ratio 9 : 1) by substituting iron-free pillars, until laboratory conditions can be properly controlled as regards movements of bodies containing iron. Moreover, it seems desirable to construct an entirely new apparatus employing materials chosen with scrupulous care in respect of magnetic properties*. At the same time it will be possible to incorporate the finer suspension mentioned earlier, and to make provision for the essential dimensions to be accurately known, thus enabling precise measurement to take the place of mere demonstration.

At present the optical magnification used is about 3800, that is, the mirror on the beam is about 190 cm. from the scale over which the light-spot moves, and 3800 mm. on the scale thus correspond to a rotation of the beam through one radian. It is probable that this magnification can be increased with advantage.

§ 5. BEHAVIOUR OF THE INSTRUMENT

As already indicated the dimensions and other constants of the apparatus are known only approximately, and cannot be determined conveniently with precision. Accordingly it is proposed now only to indicate how the apparatus behaves under roughly specified conditions. With regard to its sensitivity the introduction into one of the copper containers of a sufficiently long loosely fitting test-tube containing a few cubic centimetres of distilled water produces a deflection of about 40 mm. when the original position of the beam is approximately symmetrical. Of this about 15 mm. is attributable to the test-tube, the glass of which happens to be, like water, diamagnetic. When the beam is originally nearer the used copper container than the other the repulsion is much larger, as the force varies very rapidly with proximity. With a piece of bismuth moulded into the shape of the test-tube the repulsion is so large as to make the beam reach its limits of free movement, corresponding on either side of the central position to about 400 mm. A piece of the same $\frac{1}{4}$ -in. brass rod as was used to construct the pillars (p) displays still greater attraction. A further interesting observation is that a cylinder of aluminium on being lowered into the copper tube first repels the magnet suddenly, and thereafter slowly exhibits the attraction appropriate to its paramagnetism. The

* The cadmium-copper recommended by Kapitza and Webster (*loc. cit.*) may prove to be suitable.

explanation of the initial repulsion is the development of eddy currents in the aluminium while it is in relative motion with reference to the magnetic field of the suspended magnet. These are some examples of the efficacy on the instrument.

On the question of its behaviour as regards constancy of zero it is observed to be extremely sensitive to changes of ferromagnetic structure in its immediate neighbourhood. Any things containing iron carried on one's person make themselves very evident on approach to the instrument, and even near-by articles, such as chairs, if they contain iron nails, have to be kept in a fixed position if the zero is not to change appreciably. Still more is it necessary to avoid movements, even in neighbouring rooms, of iron objects such as retort stands, and to suppress large slow changes of current in inductive circuits.

The evidence so far obtained is, however, that if no such magnetic changes occur the mere fixed presence of iron or of constant direct currents in the neighbourhood is not objectionable. (Rapidly alternating currents are, of course, always ineffective having regard to the long period of the suspension.) Observations in the Imperial College laboratory on a Sunday morning, for example, showed a zero constant to within 1 mm., proving that temporal changes of magnetic field of a character uniform enough in space, find the instrument irresponsive, as, indeed, theory predicts. This refers in practice not merely to the diurnal variations of the terrestrial magnetic field and magnetic storms, but to those still widespread enough magnetic fluctuations due to the District Railway at South Kensington. One finds no evidence of those spasmodic fluctuations so noticeable in the use of that relatively insensitive instrument, the Kew magnetometer. It seems reasonably certain that given rigid control over artificial magnetic changes in the immediate neighbourhood, and with proper design of the modified apparatus, we can anticipate a zero constancy comparable with that displayed by the Eötvös gravity instrument, while at the same time taking advantage of the full sensitivity available, probably 100 times that now used. This will imply the feasibility of employing a weaker magnet in the suspension, so that the relation between field and intensity of magnetization can be determined down to fields of a few gauss, even in the cases of gases.

§ 6. ADVANTAGES OF THE SYSTEM

Kapitza and Webster* have already discussed in some detail the advantages of a system in which the magnet, instead of the specimen as in the Curie balance, is suspended. These apply in the main also to the present arrangement. The practicability of making the measurement a null one is very important, as it surmounts the difficulty of the precise measurement of the small and variable separation distances which is necessary in the deflection method. It would clearly be easy to incorporate in the present apparatus also suitably disposed coils of wire, so that by the passage of a certain readily measurable current the magnetic effect of the specimen under investigation could be balanced.

The control of the physical conditions of the specimen, as regards temperature,

* *Loc. cit.*

for example, is also within the scope of experiment; and, although the measurements would be in the main comparative, an approximation to absolute determinations would evidently be possible. For example, experiments made with the present imperfect instrument showed that when a volume of water approximately spherical and of radius about 1.28 cm. was placed with its centre about 1.80 cm. from the rough location of the magnet pole of 50 c.g.s. units, a deflection of 35 mm. was obtained. (The thin glass container showed a negligible effect.) This implies a force of repulsion of approximately 5.77×10^{-8} dyne, taking the effective torsional coefficient to be nine times that of the main suspension, i.e. 1.44 dyne-cm. per radian, the half length of the beam 2.3 cm., and the optical magnification 3800 mm. per radian. Equating this to the force calculated for the above conditions on p. 496, we obtain

$$8.48 \times 10^3 \kappa = -5.77 \times 10^{-8}$$

or

$$\kappa = -6.8 \times 10^{-7} \text{ e.m.u.}$$

No stress is laid here on the fact that this value is near the usually accepted value of -7×10^{-7} e.m.u. for intense magnetic fields. There is too much uncertainty in the present apparatus as to the precise values of the small dimensions involved. The location of the magnet pole is also not known accurately, and the assumption of its being a point pole is surely too bold. Moreover, it remains yet to be proved or otherwise that the susceptibility is the same in strong and weak fields. All that can be affirmed now is that it is of the same order.

§ 7. FURTHER USE OF THE APPARATUS

Besides being useful for demonstration purposes the present comparatively insensitive instrument will serve as a means of controlling the components to be used in later models of greater accuracy and sensitivity. It will enable exacting tests to be made of the magnetic properties of all materials proposed to be incorporated, and thus ensure freedom of the suspended system from spurious control such as has become evident in the first example.

§ 8. APPLICATION TO CURRENT-MEASUREMENT

The practicability of using current control in these sensitive measurements of magnetic field distortion immediately suggests that the system under discussion provides a basis for the construction of a new form of galvanometer capable of measuring extremely small currents. It is to be noted that the use of only one magnet secures complete astaticism, since no matching of different magnets is involved. The suggested galvanometer would be of the moving magnet type, and it would be convenient to modify the suspension described earlier by making horizontal (instead of nearly vertical) the axis of the suspended magnet, and fixing the counterpoise to the appropriate position on the other side of the beam. The theory as regards behaviour in a uniform field and immunity from large-scale

temporal changes of field is thus in no way modified. The normal position of the beam would be chosen to be as nearly as possible at right angles to the magnetic meridian, since the magnet, preferably shorter than 5 in., say 2 in., would remain always with its magnetic axis along the meridian. The arrangement would be as in figure 5. Two coils or solenoids with axes coincident with that of the magnet would be disposed as shown, as closely as freedom of movement of the magnet would permit. The sense of winding would be such that the magnetic forces on the two poles due to the current in the solenoids would conspire to turn the beam in the same direction. We may see from the following calculation what may be

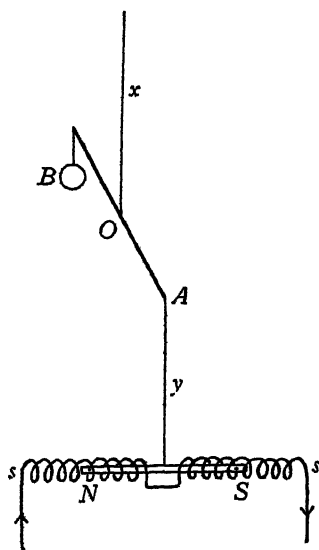


Figure 5. *NS* magnet, *B* counterpoise, *ss* current-bearing solenoids, $OA=b$, x main suspension, y subsidiary suspension.

anticipated in the matter of sensitivity. The force on each pole is $\frac{4}{10}\pi nmC$, where C is the current in amperes, and n the number of turns per cm. on the solenoids. This force, doubled, at the end of an arm of length b , gives a force moment $\frac{4}{5}\pi n\pi bC$, and if θ is the twist imparted to the central suspension, and τ the effective torsional coefficient, equilibrium corresponds to

$$\tau\theta = \frac{4}{5}\pi n\pi bC.$$

If M is the optical magnification, and d the scale deflection $\theta = d/M$, so that

$$C = 5\tau d/4\pi n\pi bM.$$

As an example of practically possible values we may take the magnet to be 2 in. of $\frac{1}{8}$ in. diameter 15 per cent cobalt steel, which will weigh a little over 3 gm., and provide poles about 50 c.g.s. units approximately 4 cm. apart. (This leaves ample room for the solenoids in which it would be desirable for the magnet poles normally to occupy the centres.) A value of τ of 0.02 dyne-cm. per radian would be

considerably larger than necessary, but we assume this. Finally, with $b = 2$ cm., say, $n = 10$ turns per cm., and $M = 4000$ mm. per radian, we obtain

$$\begin{aligned}\frac{C}{d} &= \frac{5 \times 0.02}{4\pi \times 10 \times 50 \times 2 \times 4000} \text{ A./mm.} \\ &= 2 \times 10^{-9} \text{ A./mm. approximately.}\end{aligned}$$

This gives the anticipated sensitivity in a galvanometer which, by reason of the small number of turns of copper wire assumed, would have a negligible resistance. With n sufficiently multiplied by using finer wire, a sensitivity of 100 or perhaps even 1000 times as great could presumably be obtained.

Such a galvanometer would have, however, an unusually long time period—in the above case about 220 sec.—so that it could be applied only to the detection and measurement of very slowly varying currents. As in all galvanometers quick action implies sacrifice of sensitivity. By making $b = 2$ mm., instead of 2 cm., for example, the time period would be reduced to 22 sec., while the sensitivity would also be reduced in the same proportion of ten to one.

DISCUSSION

Dr H. SHAW. It is interesting to note that although the Eötvös torsion balance, and the gravity gradiometer which suggested this apparatus to the author, are essentially field instruments, the new instrument, at any rate for the present, appears to be of the laboratory type. I am also interested to hear of the difficulties which have been encountered as a result of the magnetic nature of brass, and which bear out my own experience. On occasions I have found the magnetism of the brass to be sufficiently large to produce effects which completely masked its gravitational effect.

I should like to ask the author whether he has yet made any quantitative measurements.

Dr L. F. BATES. The author has shown us a delightfully simple piece of apparatus and I am sure that we all look forward to hearing more concerning the behaviour of substances in weak magnetic fields. We have no right to assume that the susceptibility is a constant until it has been proved to be so for these low fields. One of the most remarkable things about the apparatus is that a vertically suspended magnet, which must have some horizontal component of its magnetic moment, can behave so well. Indeed, I am surprised that the author has not needed to trouble about this horizontal component. If he should need to do so with the new form of the apparatus, I commend to him the "gallows" which Chattock and I used for getting rid of such a component some years ago.

The question of electromagnetic control is an intriguing one. I note that the author speaks of a system of coils for this purpose. Actually, I think he will find when he settles down to this particular problem that he will obtain all the control required, simply by using a single long straight wire placed parallel to the cross-piece of the torsion balance and at a little distance below the magnet, but not

vertically below it. The lines of force will be circles concentric with the wire and, obviously, the lower pole will be acted upon by a greater force than the upper one.

Dr L. HARTSHORN said that for the purpose of absolute measurements it was necessary to know the permeability of the substances of which coil formers are made. It had been found that both marble and pyrex are diamagnetic, to an extent which could not be neglected in precision work, and it is probable that the author's instrument would be of considerable value in this direction, since it appears to be more sensitive than existing methods and also to be applicable to finished coils.

Dr F. D. SMITH. The magnetic torsion balance described in this paper appears to have great possibilities in its present form and also to afford scope for improvement in the future. It is interesting and profitable to examine the conditions that make for an even better performance—that is, increase of sensitiveness with reduction of periodic time.

The formula for the deflection θ in terms of the force F acting on the pole is

$$\theta = Fb/\tau \quad \dots\dots(1),$$

where b is the arm of the balance and τ is the stiffness of the suspension: τ' is assumed to be small in comparison with τ . The resonance angular velocity ω is given by

$$\omega^2 = \tau/I \quad \dots\dots(2),$$

where I is the moment of inertia of the suspended system. These equations give

$$\theta\omega^2 = Fb/I \quad \dots\dots(3),$$

where $\theta\omega^2$ is a factor of merit since increase of θ and ω are advantageous. In fact, the design should be such that $\theta\omega^2$ is a maximum. Let us see what factors contribute to increase this product.

In cases where the magnet pole is near the sphere, that is, where s (or a/c) is nearly unity,

$$\sinh 2y - 2y \approx 2c^2/(c-a)^2 \quad \dots\dots(4),$$

whence

$$F = \frac{1}{4} \cdot \frac{\mu - \mu'}{\mu + \mu'} \cdot \frac{m^2}{\mu'} \cdot \frac{1}{(c-a)^2} \quad \dots\dots(5),$$

where m is the strength of the magnet pole, μ is the permeability of the substance under examination and μ' is the permeability of air; $(c-a)$ is the distance between the pole and the surface of the sphere. This expression, which is derived from the formula given by the author, can be identified as the formula for the force of attraction between the pole and a thick extensive plane slab of material at distance $(c-a)$ and having permeability μ . It seems that the shape of the body under examination does not matter since the same formula applies for a sphere and a slab provided always that the pole is close to them. In fact, only the material in the immediate vicinity of the pole contributes materially to the mechanical force.

The author uses 15 per cent cobalt steel for his magnet, the ratio of length to diameter, on which the demagnetizing effect of the poles at the ends depends,

being 40 to 1. A lighter magnet results from the use of steel of better quality, as the following table indicates.

Steel	Coercive force	Length/ diameter
15 per cent cobalt steel	190	40
35 per cent cobalt steel	240	32
M. K. aluminium steel	700	11

It has been assumed, as a rough approximation, that the ratio n of length to diameter varies inversely as the coercive force for a given intensity of magnetization I_r . The new Japanese magnet steel, now available in England, enables the mass of the suspended system to be cut down to one quarter, the periodic time being thereby halved. If the radius of the circular section of the magnet is r , the length is $2\pi r$ and the formula for the moment of inertia of the suspended system becomes

$$I = 4\pi\rho n r^3 b^2 \quad \text{.....(6),}$$

where ρ is the density of the magnet.

Writing $m = \pi r^2 I_r$, we reduce equation (3) to

$$\theta\omega^2 = \frac{\pi}{16} \cdot \frac{\mu - \mu'}{\mu + \mu'} \cdot \frac{I_r^2}{\rho n} \cdot \frac{r^2}{(c - a)^2} \cdot \frac{1}{br} \quad \text{.....(7).}$$

We wish to make $\theta\omega^2$ a maximum. The term $\frac{\mu - \mu'}{\mu + \mu'} \cdot \frac{1}{\mu'}$, represents the magnetic quality of the substance under test and is not under control. The term $I_r^2/\rho n$ represents the magnetic quality of the magnet; since it must be as large as possible, n must be small, that is, the magnet must be short and thick; the density must also be small and, though the actual density of the magnet steel is not under control, it is possible to reduce the effective density by making the magnet of dumb-bell shape with enlarged ends. The term $r^2/(c - a)^2$ is a measure of the proximity of the magnet to the substance under test; since r must be less than $(c - a)$, it has a maximum value of unity. The final term $1/br$ determines the scale of size of the balance; to make this term large, the arm of the balance b and the radius of the magnet cross-section r must be small. It seems that the magnetic torsion balance should be made as small as possible, the practical limit being set by the fineness and permissible length of the suspending wires. This conclusion is in accordance with the historical development of other electrical instruments, for example the quadrant electrometer and its minute modern counterpart, the Lindemann electrometer.

On the basis of these calculations I venture to predict that the magnetic torsion balance may be greatly reduced in size with consequent increase of sensitiveness or quickness of response, or both.

Mr J. E. CALTHROP. I gather that the suggested galvanometer would have a very long period. One of its possible uses might therefore be to demonstrate the existence of very slow electric oscillations of a period of a few seconds. Such an

experiment has been described by Prof. R. W. Pohl of Göttingen. The oscillations were produced by allowing a charged condenser to discharge through a very large inductance, and the period of the oscillations was observed by means of a galvanometer of special design and having a period of about 35 sec. For instructional purposes such an ocular demonstration would be of great value.

Dr A. B. WOOD. The direct applications of the instrument to the measurement in the laboratory of the magnetic properties of materials make it extremely valuable, apart altogether from its possible application as a field instrument, for which purpose it was originally designed.

In his theoretical treatment on page 395 the author considers the forces acting on a single pole of the suspended magnet. What is the resultant effect of the two opposite poles? How is the sensitivity affected by the distance apart of the poles, and by the length of the magnet relative to the size of the specimen?

If further sensitivity is at any time required, it seems possible that the new Japanese aluminium steel, supplied by Lucas of Birmingham, may prove superior to cobalt steel for the suspended magnet, having a considerably greater coercive force for a given volume.

The demonstration gave me the impression that extremely few materials may be regarded as non-magnetic and we shall look forward to a further paper by the President in which he reveals the non-magnetic substance to which he referred so mysteriously during the demonstration.

AUTHOR'S reply. It will be convenient if I reply first to Dr Wood's questions, as the answers have a bearing on some comments I have to make on Dr F. D. Smith's contribution to the discussion. If the magnet is long in comparison with its distance from the specimen, itself also supposed relatively small, the pole remote from the specimen experiences a negligible force, since something like an inverse fifth-power law operates. But if the specimen is large—if, for example it extends parallel to the magnet over its whole length—the resultant effect would clearly be twice that due to a single pole. The forces also depend on the shape of the specimen, although if it is very close to the magnet pole the shape is relatively unimportant, as Dr F. D. Smith has pointed out.

As I have already indicated I have preferred to use the lower pole for electro-magnetic damping, and not to procure increased sensitivity. This implies a practical limit to the extent to which the magnet may be shortened. Moreover, although I have not calculated precisely the forces operating when the inter-polar distance is diminished, the problem being too difficult, I am convinced that ultimately such shortening will decrease the resultant force, because of the tendency for more of the lines of force to pass directly from pole to pole without penetrating the specimen. At the same time I believe that some reduction of length would be advantageous in reducing the period in the manner which Dr F. D. Smith suggests.

I am glad to have from both Dr Wood and Dr F. D. Smith the information regarding the properties of the new aluminium steel. Its greater coercive force will permit the reduction of length contemplated for the magnet, and if its greater

coercive force implies—I am not sure of this—that the remanent magnetism will be greater also, the new steel will afford still greater advantages.

I welcome Dr F. D. Smith's clear exposition of the questions of sensitivity and quickness of response, which in the present model are not as good as they might be. The instrument was in the first instance designed as a means of measuring gradients of the earth's field, and in its present adaptation to the measurement of susceptibility somewhat different conditions apply, so that suitable modifications must be made in new designs. I think Dr Smith's general conclusions are correct, and correspond not only to those for the electrical instruments to which he refers, but also to those reached by Boys in relation to his gravity balance to which my instrument is more nearly akin. But I am not sure how far it will be possible in practice to adhere to the theoretical argument, which assumes that it will always be possible to obtain materials of the properties and dimensions demanded by the theory. There will be, as Dr Smith anticipates, a practical limit to the fineness of the suspending wires, determined by the skill of the construction and the delicacy of handling on the part of the user. I expect also that spurious movements due to air convection will become more troublesome with very light suspended systems. But there is clearly much room for improvement on the lines Dr Smith has suggested, especially with regard to quick action, since the sensitivity already seems to be ample.

In reply to Dr Shaw: I have made some rough comparisons which show that substances have approximately the same relative susceptibilities in weak as in strong fields. I anticipate being able to make the measurements more precise when the null method indicated is employed. In this connexion I am much indebted to Dr Bates for his suggestion that a single straight current-bearing wire outside the case of the apparatus will serve. I have since tried this, and it works admirably with currents of the order of milliamperes. I place the wire under the apparatus in the vertical plane containing the beam. The wire is in fact about 6 cm. vertically below the lower end of the magnet. I do not understand why Dr Bates says it should not be quite vertically below it. As at present arranged it produces a horizontal force on the pole perpendicular to the plane of the beam, which is what we require.

Dr Bates' other suggestion also interests me very much, but it applies more to the original attempt to design a magnetic gradiometer which I described in my presidential address. In the present use of the instrument I actually prefer the magnet to have a definite horizontal component of moment, so that it will take up a nearly constant azimuth. When I have time to revert to the first project I shall have to examine whether the Chattock and Bates "gallows" will fulfil sufficiently the extraordinarily stringent demands for the elimination of control by the earth's horizontal field.

THE APPLETON-HARTREE FORMULA AND DISPERSION CURVES FOR THE PROPAGATION OF ELECTROMAGNETIC WAVES THROUGH AN IONIZED MEDIUM IN THE PRESENCE OF AN EXTERNAL MAGNETIC FIELD. PART 2: CURVES WITH COLLISIONAL FRICTION

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ABSTRACT. This paper presents curves given by the Appleton-Hartree formula and illustrating the effect of collisional friction on the indices of refraction and attenuation for the propagation of electromagnetic waves through an ionized medium in the presence of an external magnetic field. Four typical frequencies have been chosen for the calculations, one from each of the classes into which the frequencies fall when collisional friction is absent, as described in part 1. The corresponding wave-lengths are 80, 240, 400 and 1000 m. The various stages in the effect of increasing collisional friction have been found to be usefully represented by collisional frequencies of 10^5 , 10^6 , 10^7 c./sec. and curves are given showing the indices of refraction μ_r and attenuation κ_r , ($r = a, b$), the real part and the imaginary part of M_r^2 or $(\mu_r - i\kappa_r c/p)^2$, and the polarizations of the basic modes as functions of the electronic density for each of the four frequencies and collision frequencies named. The process of evaluation of M_r and of the polarization is described. It is confirmed that a critical collision frequency ν_c equal to $p_T^2/2p_L$ gives a transition from propagation with the characteristics of that transverse to the magnetic field (occurring when $0 < \nu < \nu_c$) in which the polarization is linear when the electron-density $N = 3\pi mf^2/2e^2$ (the polarization of each of the basic modes changing sign on passing through linearity), to that with the characteristics of longitudinal propagation (occurring when $\nu > \nu_c$) in which the polarization is never linear and retains its sign for all values of N in both modes.

The attenuation and absorption are found to be, in general, greater for the right-handed component than for the left-handed component, with the direction of magnetic field appropriate for down-coming waves in the northern hemisphere. A table is given showing the polarization of the component having the greater index of attenuation and the greater value of $\kappa\mu$ with varying electronic density. The use of the dispersion curves in the interpretation of propagation phenomena is discussed; consideration of the values of the indices of attenuation in addition to those of the indices of refraction leads to the general conclusion that the lower boundary of the Kennelly-Heaviside layer must be sharp in the optical sense and that reflection of long waves occurs at this boundary at the same height, in general, as that of much shorter waves.

§ 1. INTRODUCTION

THE first part of this paper* was concerned with a discussion of the Appleton-Hartree formula giving the indices of refraction and attenuation for propagation of electromagnetic waves in an ionized medium with an external magnetic field. In this formula the symbol $M = \mu - i\kappa c/p$; μ is the index of

* *Proc. Phys. Soc.* 45 245-64 (1933); subsequently referred to as "part 1."

refraction; $i = \sqrt{-1}$; κ the index of attenuation; c is the velocity of electromagnetic waves in vacuo; $p = 2\pi \times$ the frequency of the waves under consideration; $\alpha = -p^2/p_0^2 - \frac{1}{2}$; $\beta = pv/p_0^2$; $p_0^2 = 4\pi Ne^2/m$; $\nu = 1/\tau$ and is the frequency of collision of electrons with molecules; N is the electron-density; e, m are the charge and mass of an electron; $\gamma_T = p p_T/p_0^2$; $\gamma_L = p p_L/p_0^2$; $p_T = H_T e/mc$; $p_L = H_L e/mc$; and H_T, H_L are the components of magnetic field perpendicular to and along the direction of propagation. With these symbols the formula was as follows

$$M^2 = \left(\mu - \frac{i\kappa c}{p} \right)^2 = 1 + \frac{2}{2(\alpha + i\beta) - \frac{\gamma_T^2}{1 + \alpha + i\beta} \pm \left(\frac{\gamma_T^4}{(1 + \alpha + i\beta)^2} + 4\gamma_L^2 \right)^{\frac{1}{2}}};$$

the discussion of part 1 was restricted to the phenomena holding in the absence of collisional friction between the free electrons, which are assumed to be the cause of the dispersion, and the molecules of the surrounding gas. This implied a zero value of the collision frequency ν and therefore of the quantity β ; the expression for M^2 was purely real and the modes of propagation which could occur were (i) and (iii) described in part 1, § 2, pp. 248-50. When collisional friction is present ν and β are no longer zero and the expression for M^2 becomes complex; neither μ nor κ can be zero (with the exception that $\kappa = 0$ when $N = 0$) and the mode of propagation is the second one described in part 1, § 2, in which progressive waves are propagated but suffer exponential diminution of amplitude, which falls to $1/e$ of its value in a distance κ^{-1} . This type of propagation is associated with true absorption of energy, the amount being proportional to the product $\mu\kappa^*$. For values of ν of the order of 10^5 per sec. or less, the values of μ and κ for certain ranges of values of the electron-density approach very nearly to zero, and the presence of friction merely has the effect of removing the infinities in the dispersion curves and rounding off the corners slightly; so that the dispersion curves given in part 1 may, as was mentioned in the discussion, be used in the interpretation of propagation phenomena when the value of ν is estimated to be of the order of 10^5 per sec. or less. As ν increases, the steep maxima and minima of the dispersion curves are rapidly smoothed out and the curves for different wave-frequencies become more similar to one another; at the critical collision frequency ν_0 or $p_T^2/2p_L$ the propagation changes from the type described in part 1, § 4, p. 263 (in which the polarization of each basic mode is linear when $N = \frac{2}{3}\pi m f^2/e^2$ and changes there from left-handed to right-handed or *vice versa*) to a type approximating to that of transmission along the external magnetic field, in which the polarization is never linear and that of either basic mode retains its sense of rotation for all values of N . This confirms the conclusion of E. V. Appleton and G. Builder†. For still greater values of ν , the curves for μ and κ as functions of N for any given frequency tend more and more to linearity and approach the values 1 and 0 respectively; these are their limits for an infinite degree of friction, in which case the medium exerts no refractive or dispersive effect upon the waves passing through it, since the electrons are then unable to execute forced oscillations.

* Cf. part 1, p. 249.

† *Proc. Phys. Soc.* 45, 217-18 (1933).

The dispersion curves given in this paper illustrate the effect of various degrees of friction at different wave frequencies. They have been drawn from calculations* of M_r^2 as a function of N , the electron density, with the value of the imposed magnetic field used in part 1 and values of ν , the collision frequency, increasing from zero, where M_r^2 is $(\mu_r - i\kappa_r c/p)^2$.

Four typical wave-frequencies have been chosen, one from the range of each of the four classes of dispersion curve described in part 1; the corresponding wavelengths are 80, 240, 400 and 1000 m., for which the dispersion curves for $\nu = 0$ were given in part 1. The values of ν which have been found to be representative of different orders of magnitude of the effect of friction are 10^5 , 10^6 , and 10^7 c./sec. Friction exerts practically no influence on propagation, even of the longer waves, until the collision frequency is of the order of the frequencies used in practical wireless communication (about 100 kc./sec.). When ν has reached a value of 10^7 c./sec., μ and κ are practically linear functions of N for any one frequency, and the type of propagation is almost exactly longitudinal. $\nu = 10^6$ c./sec. gives an intermediate value.

§ 2. EVALUATION OF M_r AND CRITICAL COLLISION FREQUENCY

In calculating the values of M_r , the first quantity to be evaluated is

$$p_0^4 [\gamma_T^4 + 4\gamma_L^2 (1 + \alpha + i\beta)^2]^{\frac{1}{2}} = [p^4 p_T^4 + 4p^2 p_L^2 (\frac{2}{3}p_0^2 - p^2 + ip\nu)^2]^{\frac{1}{2}};$$

it is from the alternative signs to be prefixed to this square root that the two values M_a and M_b are obtained. In part 1 the quantity under the square root sign was always positive, being the sum of the squares of two real quantities; the values M_a and M_b corresponding to the ordinary and extraordinary waves were given by the positive and negative signs respectively. With β and ν unequal to 0, the quantity under the square-root sign is complex and the vector OP representing it moves away from the real axis into the Argand diagram, as shown in figure 1.

The square root of the complex quantity represented by OP , or $re^{i\theta}$, where $-\frac{\pi}{2} < \theta < \frac{\pi}{2}$, is represented by the two vectors OP' or $r^{\frac{1}{2}}e^{i\frac{\theta}{2}}$ and OP'' or $r^{\frac{1}{2}}e^{i\frac{\theta}{2}(\theta+2\pi)}$.

As OP tends to the x -axis ($\theta \rightarrow 0$), OP' tends to lie along the positive direction of Ox and OP'' along its negative direction, so that, for continuity with the case of zero friction, we must, for small values of β and N , take OP' as the root corresponding to M_a and OP'' as that corresponding to M_b ; i.e. the roots giving M_a and M_b are those whose real parts are positive and negative respectively.

The curve described by P in the Argand diagram is given by

$$\begin{cases} x = p^4 (p_T^4 - 4p_L^2 \nu^2) + 4p^2 p_L^2 (\frac{2}{3}p_0^2 - p^2)^2, \\ y = 8p^2 p_L^2 \nu (\frac{2}{3}p_0^2 - p^2). \end{cases}$$

* The calculations have included the term which, according to Hartree, expresses the discreteness of the scattering centres, so that the equation $\alpha = -p^2/p_0^2 - \frac{1}{2}$ has been used as against the equation $\alpha = -p^2/p_0^2$ which holds in the absence of this term. The inclusion of the term is still a debatable matter; if it be omitted, $N = \pi m f^2 / e^2$ should replace $N = \frac{2}{3} \pi m f^2 / e^2$ throughout.

The parameter N , the variable electronic density, occurs only in the quantity $p_0^2 = 4\pi Ne^2/m$; eliminating $\frac{2}{3}p_0^2 - p^2$, we find that the locus of P is the parabola

$$y^2 = 16p^4 p_L^2 \nu^2 [x - p^4 (p_T^4 - 4p_L^2 \nu^2)]$$

with axis along Ox .

For N and therefore $p_0 = 0$, $y = -8p^5 p_L^2 \nu$, a negative quantity, so that the parabola begins at a point P below the axis of x . Its vertex A is at the point $[p^4 (p_T^4 - 4p_L^2 \nu^2), 0]$ where $p_0^2 = \frac{2}{3}p^2$ or $1 + \alpha = 0$.

As $N \rightarrow \infty$, both x and y become positive and increase without limit. If $\nu < \nu_c$, the x -coordinate of the vertex is positive, figure 2.1; if $\nu = \nu_c$, it is zero, figure 2.2, and if $\nu > \nu_c$ it is negative, figure 2.3. The vectorial square root OP_a of OP corresponding to M_a must, for continuity with the case $\nu = 0$ for small values of N , be such that its real part is positive in every case when $0 > \theta_p > -\pi$ where θ_p is $\angle xOP$; in figure 2.1, θ_p steadily increases to zero and positive values and the real part of OP_a remains positive for all N ; P_a moves along the curve $P_a A_a Q_a$. In figure 2.2, $\nu = \nu_c$; A , A_a and A_b have moved to coincidence at O and the path of P_a is $P_a O Q_a$. The real part of OP_a is still always positive. Figure 2.3 illustrates the case where $\nu > \nu_c$; $O A_a$ now lies along the negative y -axis and, for continuity, the curve $P_a A_a$ must continue with increasing N into the left half-plane to points such as Q_a . Thus when $\nu > \nu_c$ and $1 + \alpha > 0$, the square root of OP corresponding to M_a must be taken with a negative real part. The paths $P_b A_b Q_b$ of the end of the vector giving the square root corresponding to M_b are shown as dashed lines in the figures.

Considerations of continuity have thus made clear the rule which must be adopted for determining which of the signs prefixed to the real part of the square root gives M_a^2 and which M_b^2 ; the positive sign must be chosen for M_a^2 except when $\nu > \nu_c$ and $1 + \alpha > 0$, when the negative sign must be taken. By definition, μ_r and κ_r ($r = a, b$) are always positive, so that the remainder of the calculation is straightforward. The curves for μ_r and κ_r are shown in figure 3. Those for the real part of M_r^2 are shown in figure 4 and those for the imaginary part of M_r^2 in figure 5.

The critical collision frequency ν_c , i.e. $p_T^2/2p_L$ or $(H_T^2/2H_L)(e/mc)$, at which the dispersion curves change so fundamentally, depends on the values of e , m and c and further only on the value of the external magnetic field and its inclination to the direction of wave-propagation. It is remarkable that it is independent of the wave-frequency and of the electronic density. For the value of the earth's magnetic field at Slough (for which the curves given here have been calculated) and vertical propagation, the value of ν_c is found to be 6.86×10^5 which would correspond to a wave-length of 437.3 m.

When $\nu = \nu_c$, the parts of the dispersion curves beyond

$$N = \frac{2}{3}\pi m f^2 / e^2 \text{ (i.e. } 1 + \alpha = 0 \text{)}$$

appear to change over, so that points where μ_a was very nearly zero when $\nu < \nu_c$ are, when $\nu > \nu_c$, on the curve for μ_b and *vice versa*. This is most clearly seen in the curves of figure 4, which show the real part of M_r^2 . This is the form in which the dispersion curves given in part 1 were drawn; with $\nu = 0$, M_r^2 was purely real and μ_r and κ_r could be immediately deduced by taking the square root of M_r^2 . The

curves for $\nu = 10^5$ c./sec., figures 4.11, 4.21, 4.31, 4.41, are evidently the curves of part I with the infinite branches joined up so that the curves become continuous. $\nu = 10^6$ c./sec., figures 4.12, 4.22, 4.32, 4.42, is already above $\nu = \nu_0$ and the branches above $N = 3\pi mf^2/2e^2$ ($1 + \alpha = 0$) have crossed over though there are still kinks in the curves near $N = 3\pi mf^2/2e^2$. For $\nu = 10^7$ c./sec. the effect of friction predominates and the kinks have almost disappeared; it is already clear that the curves tend to $M_r^2 = 1$ as $\nu \rightarrow \infty$.

§ 3. POLARIZATION

The formula giving the polarization was stated in part I, §2 in the form

$$-\frac{E_x}{E_y} = \frac{H_y}{H_x} = \frac{i\gamma_L(1 - M^2)}{1 + (\alpha + i\beta)(1 - M^2)},$$

where the incident wave is propagated along Oz and the external magnetic field has components H_L, H_T along Oz and Ox respectively. Hence, when M_r^2 has been evaluated, the polarization may be deduced. When collisional friction is present, the ratio $-E_x/E_y$ or H_y/H_x is no longer evaluated as a purely imaginary quantity, but contains a real part also; the principal axes of the polarization ellipses no longer lie along Ox and Oy but are rotated through an angle ψ . It is still true that the product $(H_y/H_x)_{M_a}(H_y/H_x)_{M_b} = 1$, so that the major axes of the ellipses are again mutually perpendicular and the ellipticities are the same, while the directions of description are opposite. Figure 6 illustrates the crossed polarization ellipses corresponding to M_a and M_b and shows how the angles ψ and θ are defined geometrically. As in part I, $\theta = 0$ corresponds to linear polarization; positive values of θ correspond to an anti-clockwise (left-hand) direction of rotation viewed along the direction of propagation, and negative values of θ to clockwise (right-hand) rotation. $\theta = \pm 45^\circ$ correspond to left- and right-hand circular polarization respectively.

Let $iE_y/E_x = A + iB$, and be calculated from the formula above. The ellipse described by the end of the electric vector in the (x, y) plane is then given by

$$x = E_x = \cos \omega t,$$

$$y = E_y = R \left(\frac{A + iB}{i} e^{i\omega t} \right) = B \cos \omega t + A \sin \omega t$$

or, eliminating t , $y^2 - 2Bxy + x^2(A^2 + B^2) = A^2$.

The major axis of this ellipse is inclined to Ox at an angle ψ given by

$$\tan 2\psi = 2B/(1 - A^2 - B^2)$$

and the ratio of the axes, which we will call $\tan \theta$ as in part I, is given by

$$\tan^2 \theta = \frac{(1 + A^2 + B^2) \sin 2\psi - 2B}{(1 + A^2 + B^2) \sin 2\psi + 2B}.$$

Consider the case in which $A^2 + B^2 < 1$, a relation holding for most of the calculations of the polarization corresponding to M_a^2 .

The signs of ψ and θ are then determined by the signs of B and A respectively; if $B > 0$, the part of E_y which is in phase with E_x is positive, so that ψ is a positive acute angle; if $B < 0$, ψ is a negative acute angle. For small values of N , ψ_a is found to be small and negative for all wave-frequencies; if $N > 3\pi mf^2/2e^2$ and $\nu < \nu_c$, $\psi \rightarrow 0$ again, as shown in figures 6.51 ($s = 1-4$); when $\nu > \nu_c$, ψ_a must for continuity be taken as tending to $-\pi/2$ as shown in figures 6.5t ($s = 1-4$, $t = 1-3$).

The sign of θ is determined by that of A , which gives the part of E_y out of phase with E_x ; if $A < 0$, $\theta < 0$ and rotation from E_x to E_y is clockwise or in a right-handed direction, whereas if $A > 0$, $\theta > 0$ and the rotation is anti-clockwise or left-handed (looking along the positive direction of propagation of the waves). For small values of N , the ordinary and extraordinary waves are found to be left- and right-handedly polarized respectively, as they were for the case of zero friction discussed in part 1. If $\nu < \nu_c$, the numerical value of θ starts at 45° when $N = 0$ and decreases until when $N = 3\pi mf^2/2e^2$ ($1 + \alpha = 0$), $\theta = 0$ and the polarization is linear, corresponding to a real value of the ratio H_y/H_x . When $N > 3\pi mf^2/2e^2$, θ increases numerically again to 45° ; the polarization of the ordinary wave corresponding to M_a is now right-handed and that of the extraordinary wave, corresponding to M_b , is left-handed. $|\psi|$ decreases again from its maximum value when $N = 3\pi mf^2/2e^2$ to zero when $N = \infty$, where the waves are circularly polarized. Thus when $\nu < \nu_c$ the polarization phenomena are essentially the same as when $\nu = 0$; the effect of friction is merely to rotate the polarization ellipses through the angle ψ , which is small except when ν is very nearly equal to ν_c . The fact that the polarization passes through the linear form when $N = 3\pi mf^2/2e^2$ shows that the type of propagation is similar to that transverse to the magnetic field when the polarization, viewed along the direction of propagation, is always linear.

In the case when $\nu > \nu_c$, i.e. $2p_L\nu > p_T^2$, the ratio H_y/H_x can never be purely real and the polarization never passes through the linear form. If the values of M_a and M_b when $N > 3\pi mf^2/2e^2$ are found as described in § 2, θ_a does not become zero when $N = 3\pi mf^2/2e^2$ but still has a finite positive value and, for greater values of N , remains positive, increasing again towards a limiting value of 45° as $N \rightarrow \infty$. Similarly, θ_b remains negative, so that the propagation is now of the type of that longitudinal to the magnetic field, in which the two basic modes have always circular polarization, one consistently left-handed and the other consistently right-handed for all values of N . This is the limit to which the propagation at any angle to the magnetic field tends as $\nu \rightarrow \infty$. For the value of the earth's magnetic field for which the curves here given have been calculated, this limit has been very nearly reached when $\nu = 10^7$ c./sec. and even when $\nu = 10^6$ c./sec. there is only a dip in the θ curve near the point where $N = 3\pi mf^2/2e^2$. At the critical collision frequency itself this dip would reach right down to the point where $\theta = 0$ when $N = 3\pi mf^2/2e^2$.

In the curves in figures 6.11 to 6.43 only the values of ψ and θ corresponding to M_a have been drawn as functions of N for the various wave and collision frequencies chosen. It is clear from figure 6 that the major axis of the ellipse corresponding to M_b is rotated through an angle of ψ_a from the y -axis, while $\theta_b = -\theta_a$.

The variations of θ_a and ψ_a described above are clearly shown in the curves, from which it is also evident that the general course of ψ_a and θ_a is the same for all wave-frequencies, as in part 1, and that the critical collision frequency $\nu = \nu_c$ is the decisive factor in determining the type of propagation.

Figure 7 shows the polarization when $N = 3\pi m f^2 / 2e^2$ ($1 + \alpha = 0$) as a function of the collision frequency. When $\nu < \nu_c$, $\theta_a = 0$ while ψ_a varies from 0 to -45° at $\nu = \nu_c$. When $\nu > \nu_c$, ψ_a remains constant and equals -45° while θ_a increases from 0, tending to a limit of 45° as $\nu \rightarrow \infty$.

§ 4. THE DISPERSION CURVES AND THEIR USE IN THE INTERPRETATION OF PROPAGATION PHENOMENA

The dispersion curves given in figure 3 show the calculated values of the indices of refraction, μ_r , and the indices of attenuation, κ_r ($r = a, b$), for the wave and collision frequencies selected as illustrative of the phenomena. The curves of figure 3.50 ($s = 1-4$) show the values of μ_r and κ_r for $\nu = 0$. This is an alternative presentation of the curves shown in part 1, figure 3.1, where the real quantity M_r^2 was shown as a function of N ; μ_r and κ_r are real positive quantities and, when $\nu = 0$, are zero over certain ranges of N . The occurrence of total reflection when $\nu = 0$ at the points where $\mu = 0$ was discussed in part 1, §§ 2, 6.

The curves of figures 3.51 ($s = 1-4$, $t = 1-3$) show the values of μ_r and κ_r when $\nu = 10^5, 10^6, 10^7$ c./sec. The zero and infinite values of μ_r and κ_r disappear when $\nu \neq 0$ (with the exception that $\kappa_r = 0$ when $N = 0$), and the only mode of propagation which can occur is (ii) described in part 1, § 2, in which the progressive waves suffer exponential diminution of amplitude. The curves of figure 3.51, when $\nu = 10^5$ c./sec., differ however very little from those of figure 3.50 when $\nu = 0$; μ_r very nearly = 0 over the ranges in which it was actually zero when $\nu = 0$, and for these values κ_r is large, so that the propagation phenomena when ν is of the order of 10^5 c./sec. will not differ appreciably from those described in part 1 for cases in which $\nu = 0$. When, however, ν has increased to values above ν_c , as in figures 3.52, 3.53, the propagation has changed from the transverse to the longitudinal type and the course of the dispersion curves is completely different. For frequencies above that at which $p = p_H$ (i.e. $\lambda < 227.1$ m. for the values taken in the calculations), the first value N_{b1}^* , is no longer an approximate zero of μ_b , which now has values very nearly zero at values of N near N_a ; μ_a is very nearly zero at values of N near N_{b2} , so that the ordinary and extraordinary waves may be expected to require larger values of N to reflect them, if the μ_r curves alone are taken into account; the extraordinary wave would still, however, be reflected before the ordinary one. In the case when friction is present, however, it is necessary to take into consideration also the fact that non-zero values of κ_r occur for all values of μ_r and, if κ_r is sufficiently large, the amplitude of the wave may have decreased so much before conditions of appreciable reflection are reached that the reflected energy, if any, would be too small to be detected. The amplitude falls to $1/e$ of its

* Cf. part 1, p. 261.

value in a distance κ_r^{-1} ; expressing this in terms of the quantity $\kappa_r c/p$, which is directly calculated from M_r^2 and is shown in the curves, we can estimate the attenuation from the relation

$$\kappa_r c/p = \log_e x/2\pi n,$$

where n is the number of wave-lengths *in vacuo* in which the amplitude decreases to $1/x$. Let us consider as a practical example the detection of plane 80-m. waves, reflected vertically from the ionosphere, with a receiver which will show the presence of waves whose amplitude is 0.01 of the amplitude of the waves at their incidence on the ionosphere. Remembering that they have to pass twice through the thickness of ionized medium below the reflection point*, so that $x = 10$, we find that for all frequencies this thickness may be 10 vacuum wave-lengths of the medium (i.e. $n = 10$) if $\kappa_r c/p$ does not exceed $\log_e 10/2\pi \times 10$ or 0.04 approximately.

With the curves of figure 3.12 when $\lambda = 80$ m., $\nu = 10^6$ c./sec., this value is reached when $N = 1.1 \times 10^5$ approximately, which is less than the value 2.1×10^5 of N at which the first minimum of μ_b occurs. The value of $\kappa_b c/p$ for this first minimum of μ_b is 0.415 and the amplitude of the waves is attenuated to 0.1 of its value in a space of 0.88λ or about 70 m. Thus, if the ionization N rose to 1.1×10^5 in a distance of 800 m. at a height at which the collision frequency was of the order of 10^6 c./sec., the right-handed (extraordinary) reflected component would be so much attenuated that it would not be detectable at the receiver. If the ionization increases more gradually than this, the appropriate value of $\kappa_r c/p$ will be correspondingly smaller and will be reached for very much smaller values of N . Similar arguments apply to the ordinary (left-handed) component; at the value 2.3×10^5 of N which corresponds to attenuation to 0.01 of the emitted amplitude for a layer-thickness of 800 m., μ_a is still 0.48. The approximate reflection point for the ordinary component when $\nu = 10^6$ c./sec. is that at which $N = 4 \times 10^5$, corresponding to a value 0.19 of $\kappa_a c/p$ and complete absorption would occur in a layer of this density of thickness 1.93λ or 154 m. approximately. The general conclusion is that if either component of waves of length 80 m. is to be reflected from the height where $\nu = 10^6$ c./sec., the increase in ionization to the values required for reflection must occur within a distance of the order of a wave-length, so that the reflection approximates to that studied in geometrical optics. This value of ν occurs† at a height of 90 km. approximately. Thus the lower boundary of the Kennelly-Heaviside layer must be sharp and there must be no absorbing layer of appreciable thickness below it. For if such a layer occurred at a height of say 70 km., where ν is estimated‡ to be of the order of 10^7 c./sec., the curves of figure 3.13 show that the right-handed component would be absorbed if this layer were 800 m. thick and of density $N = 2 \times 10^4$. If reflection takes place at greater heights, say 110 km., where§ ν is thought to be of the order of 10^5 c./sec., the curves of figure 3.11

* The waves are not strictly reflected from a point, but from a region in which μ approximates to zero; this will however only alter the result by a factor of the order 2, which does not affect the order of magnitude of the conclusion.

† S. Chapman, *Proc. R.S. A* 122, 373 (1929).

‡ *Loc. cit.*

§ *Loc. cit.*

give the reflection conditions in this case. Here $\kappa_r c/p$ remains very small up to the points where μ_r is very nearly zero, so that the ionization could increase more gradually to its reflection value for either component without the occurrence of appreciable absorption. It would, however, still be necessary that no absorbing layers should occur at lower levels.

A similar study may be made of the curves showing the effect of friction at lower frequencies; figures 3.21 and 3.22, for which $\lambda = 240$ m., show that the right-handed component will be completely absorbed before N approximates at all to the values required to reflect it, whereas reflection of the left-handed component may be expected from the point where $N = 3 \times 10^4$ when ν is of the order of 10^5 c./sec., or where $N = 6 \times 10^4$ (with much smaller intensity) when $\nu = 10^6$ c./sec.

Figures 3.31 and 3.32, for which $\lambda = 400$ m., show the same increased absorption of the extraordinary wave, which, even for $\nu = 10^5$ c./sec., would be absorbed before its reflection point where $N = 2.9 \times 10^4$ was reached, owing to the rise in $\kappa_b c/p$ for values of N of the order of 10^4 . When $\nu = 10^6$ the extraordinary wave would be very quickly absorbed, while if the ordinary wave succeeded in reaching the value 3×10^4 of N required to reflect it (which would be possible if the ionization gradient were sufficiently high) it would be very much attenuated. Figure 3.33 shows that reflection of 400-m. waves from ionized layers at the heights at which $\nu = 10^7$ could only occur if the layer boundary were very sharp.

The dispersion curves for which $\lambda = 1000$ m. are shown in figure 3.4; those for which $\nu = 10^3$ c./sec. and 10^4 c./sec. have also been calculated but differ very slightly from those for which $\nu = 0$. The curves in this range of frequency ($\lambda > 615.5$ m.; class 4 of part 1) differ from those for which $\lambda < 615.5$ m. in that the left-handed component is the one which is more attenuated for values of N up to $N = 3\pi m f^2 / 2e^2 (1 + \alpha = 0)$ and small values of ν . When $\nu = 10^5$ c./sec., as in the case of the curve here shown, the attenuation of the right-handed component is beginning to increase and when $\nu = 10^7$ c./sec. it is the more attenuated for all values of N , so that the behaviour for values of ν greater than ν_c is similar to that of waves of higher frequency. Figure 3.41 shows that the left-handed component of waves of length 1000 m. could, when $\nu = 10^5$, be reflected where $N = 0.167 \times 10^4$ ($1 + \alpha = 0$) and the right-handed one from where $N = 10^4$ without serious absorption; figure 3.42 however shows that the left-handed component requires when $\nu = 10^6$ a reflection density 1.5×10^4 of N , and has a strong absorption band round the point where $N = 0.167 \times 10^4$, while the right-handed component for which μ_b approximates to zero when $N = 4 \times 10^4$ is absorbed before N has reached this value. When $\nu = 10^7$ c./sec. both components are rapidly absorbed. It is therefore probable that reflection of waves of length 1000 m. occurs at the lower boundary of the Kennelly-Heaviside layer at the same height in general as that of much shorter waves, and not (except perhaps in very exceptional cases) at a height of about 50 km. as has been suggested, where ν would be greater than 10^7 and absorption very strong.

The table shows the component, right-handed (R) or left-handed (L), which

Table 1. Polarizations of components having the greater values of kc/p and ku

λ (metres)	$\nu = 10^6$				$\nu = 10^5$				$\nu = 10^4$				$\nu = 10^3$				$\nu = 10^2$			
	Range of N	Polarization (kc/p greater)	Range of N	Polarization (ku greater)	Range of N	Polarization (kc/p greater)	Range of N	Polarization (ku greater)	Range of N	Polarization (kc/p greater)	Range of N	Polarization (ku greater)	Range of N	Polarization (kc/p greater)	Range of N	Polarization (ku greater)	Range of N	Polarization (kc/p greater)	Range of N	Polarization (ku greater)
80: typical of wave-lengths from 0 to 247.1	—	—	—	—	—	—	Up to 2.62×10^4 ($1+\alpha=0$) to 2.62×10^5 Above	R	Up to 2.62×10^4 ($1+\alpha=0$) to 2.62×10^5 Above	R	Up to 2.62×10^4 ($1+\alpha=0$) to 2.62×10^5 Above	L	Up to 2.62×10^4 ($1+\alpha=0$) to 2.62×10^5 Above	R	Up to 2.62×10^4 ($1+\alpha=0$) to 2.62×10^5 Above	L	Up to 2.62×10^4 ($1+\alpha=0$) to 2.62×10^5 Above	R	Up to 2.62×10^4 ($1+\alpha=0$) to 2.62×10^5 Above	R
240: typical of wave-lengths from 227.1 to 256.2	—	—	—	—	—	—	Up to 2.84×10^4 ($1+\alpha=0$) to 2.84×10^5 Above	R	Up to 2.84×10^4 ($1+\alpha=0$) to 2.84×10^5 Above	R	Up to 2.84×10^4 ($1+\alpha=0$) to 2.84×10^5 Above	L	Up to 2.84×10^4 ($1+\alpha=0$) to 2.84×10^5 Above	R	Up to 2.84×10^4 ($1+\alpha=0$) to 2.84×10^5 Above	L	Up to 2.84×10^4 ($1+\alpha=0$) to 2.84×10^5 Above	R	Up to 2.84×10^4 ($1+\alpha=0$) to 2.84×10^5 Above	R
400: typical of wave-lengths from 236.2 to 615.5	—	—	—	—	—	—	Up to 0.96×10^4 to 0.96×10^5 Above	R	Up to 0.96×10^4 to 0.96×10^5 Above	R	Up to 0.96×10^4 to 0.96×10^5 Above	L	Up to 0.96×10^4 to 0.96×10^5 Above	R	Up to 0.96×10^4 to 0.96×10^5 Above	L	Up to 0.96×10^4 to 0.96×10^5 Above	R	Up to 0.96×10^4 to 0.96×10^5 Above	R
1000: typical of wave-lengths from 615.5 to ∞	Up to 0.1674×10^4 ($1+\alpha=0$) Above	L	Up to 0.1674×10^4 ($1+\alpha=0$) Above	L	Up to 0.1674×10^4 ($1+\alpha=0$) Above	L	Up to 0.1674×10^4 ($1+\alpha=0$) Above	L	Up to 0.1674×10^4 ($1+\alpha=0$) Above	L	Up to 0.1674×10^4 ($1+\alpha=0$) Above	L	Up to 0.1674×10^4 ($1+\alpha=0$) Above	L	Up to 0.1674×10^4 ($1+\alpha=0$) Above	L	Up to 0.1674×10^4 ($1+\alpha=0$) Above	L	Up to 0.1674×10^4 ($1+\alpha=0$) Above	L

* Though the two are very nearly equal.

† Components nearly equal.

‡ Owing to change-over of polarization of ordinary wave.

corresponds to the greater index of attenuation and also to the greater value of the quantity $\kappa_r \mu_r$, which is proportional to the amount of energy actually absorbed. In general, the right-handed component is the more attenuated and absorbed except for certain small ranges of N and for waves of length greater than 615.5 m. at very small collision frequencies. Since these long waves are reflected or absorbed before they reach the high levels at which ν is of the order of 10^4 or less, this higher attenuation of the left-handed component is of little importance in the interpretation of practical results.

The curves of figure 5, showing the values of the quantities $\mu_r \kappa_r$, display absorption maxima in certain regions of N . For frequencies belonging to classes 1 and 3 of part 1, figures 5.1, 5.3, there is only one maximum of $\kappa_a \mu_a$ and one of $\kappa_b \mu_b$ when $\nu = 10^5, 10^6$ per sec., but for those belonging to class 2, part 1, figure 5.2, there are two maxima of $\kappa_b \mu_b$ when $\nu = 10^5$ per sec. and for class 4, part 1, figure 5.4, there are two maxima of $\kappa_a \mu_a$ when $\nu = 10^5$ per sec. When $\nu = 10^7$ per sec. $\kappa_r \mu_r$ is practically a linear function of N . A logarithmic scale has been chosen for these curves, and also for those of figure 3.4 (μ_r and κ_r when $\lambda = 1000$ m.), as the range of values to be included was so great.

§ 5. CONCLUSION

The curves given in the present paper illustrate the two outstanding phenomena of magneto-ionic propagation in the presence of collisional friction:

(1) Attenuation and absorption are, in general, greater for the right-handed than for the left-handed component, with the value of magnetic field appropriate for down-coming waves in the northern hemisphere.

(2) The critical collision frequency ν_c or $p_T^2/2p_L$ gives the transition from propagation with the characteristics of that transverse to the magnetic field (occurring when $0 < \nu < \nu_c$) to that with the characteristics of longitudinal propagation (which occurs for $\nu > \nu_c$).

The curves may be used for calculations of reflection coefficient, attenuation and absorption in practical cases for the wave-lengths and collision frequencies for which they have been constructed, and they illustrate the general type of phenomenon which is to be expected at other frequencies and intermediate collision frequencies.

§ 6. ACKNOWLEDGMENTS

This work was carried out at the Radio Research Station, Slough, as part of the programme of the Radio Research Board of the Department of Scientific and Industrial Research, and is published by permission of the Board. Thanks are due to Mr R. A. Watson Watt, Superintendent of the Station, for his interest in the work and for the provision of facilities for conducting it; to Prof. E. V. Appleton and Prof. D. R. Hartree for valuable discussion, and suggestions as to the presentation of the paper; to Dr L. J. Comrie, for advice on the arrangement of the calculations; to Miss A. C. Stickland for assistance in the calculations and to Mr E. C. Slow for help in drawing the curves.

DISCUSSION

Prof. E. V. APPLETON. I do not think it is possible to over-estimate the usefulness of the author's elucidation of the magneto-ionic formula to experimental workers in this field. The wave-lengths chosen for the graphical illustration are most suitable and illustrate the variety of phenomena we are to expect.

I gather that the author agrees with the distinction between quasi-longitudinal and quasi-transverse propagation, and agrees that whether the one or the other occurs depends on the magnitude of the critical ratio $2p_L\nu/p_T^2$. Now it is found that, for the case of the penetration of the lower ionized region, propagation is of the quasi-transverse type. This means, therefore, that at a level of about 100 km., the collision frequency of electrons with gas molecules must be less than ν_0 (i.e. less than 6.86×10^5 per sec.). Prof. Pedersen's estimate for the collisional frequency at this height is 10^5 per sec.

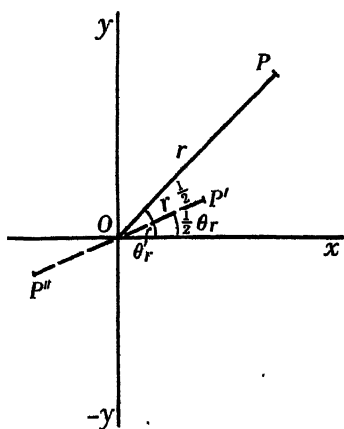


Figure 1.

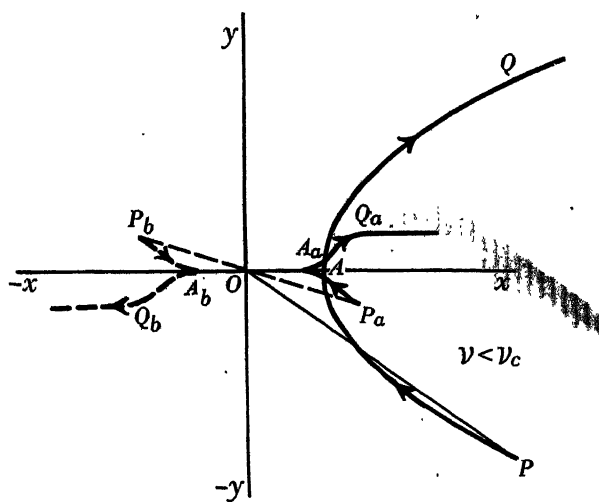


Figure 2.1.

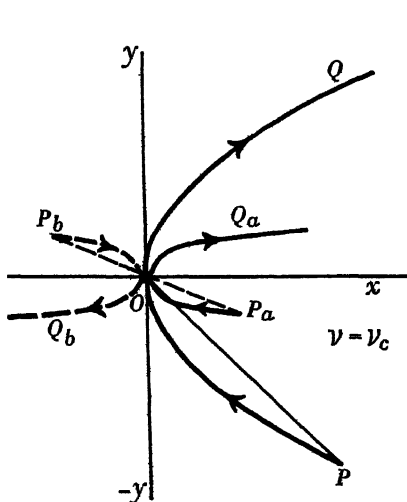


Figure 2.2.

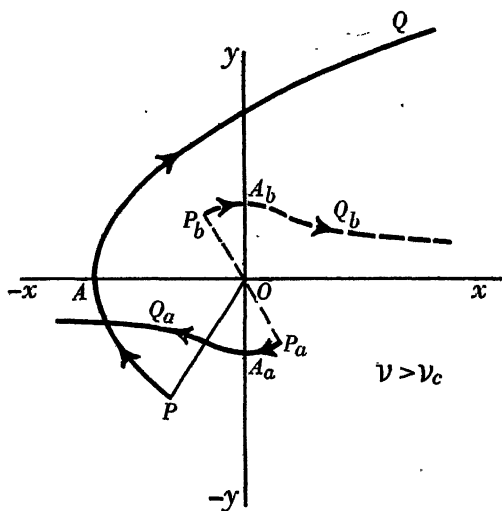


Figure 2.3.

Figure 1. Illustrating the square roots OP' , OP'' , of the vector OP .

Figure 2. The square roots of OP for: $\left. \begin{array}{l} \text{Figure 2.1, } \nu < \nu_c \\ \text{Figure 2.2, } \nu = \nu_c \\ \text{Figure 2.3, } \nu > \nu_c \end{array} \right\} \begin{array}{l} \text{— } r = a. \\ \text{--- } r = b. \end{array}$

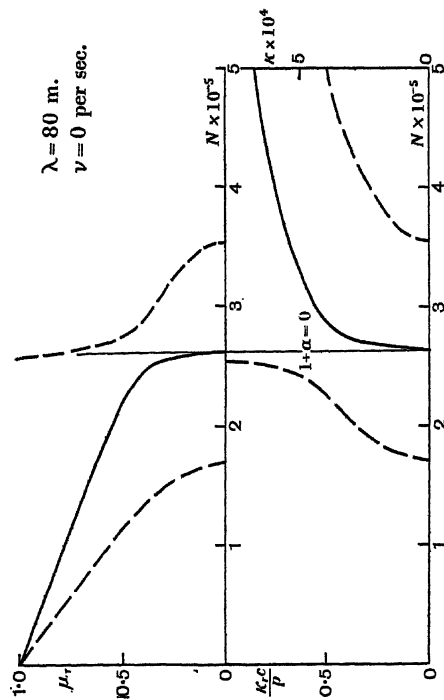


Figure 3.10.

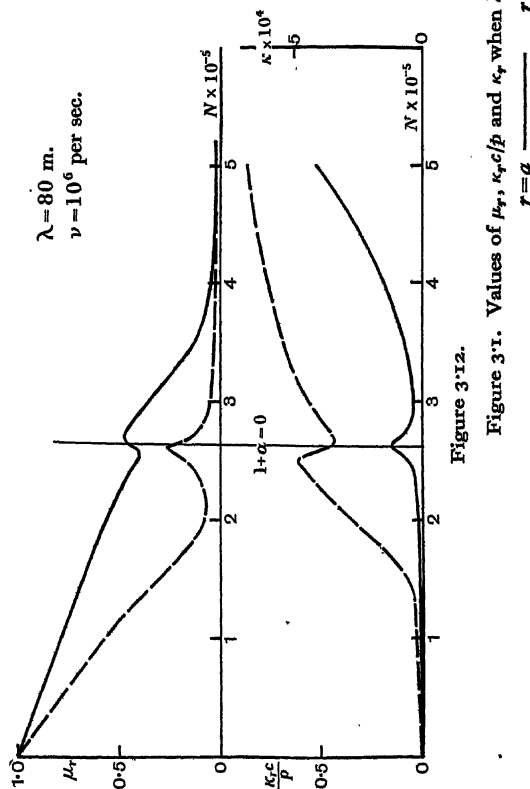


Figure 3.12.

Figure 3.1. Values of μ_r , $\kappa_r c/p$ and κ_r when $\lambda = 80$ m.; $\nu = 0, 10^6, 10^6$ and 10^7 per sec.

$r = a$ ——— $r = b$ - - -

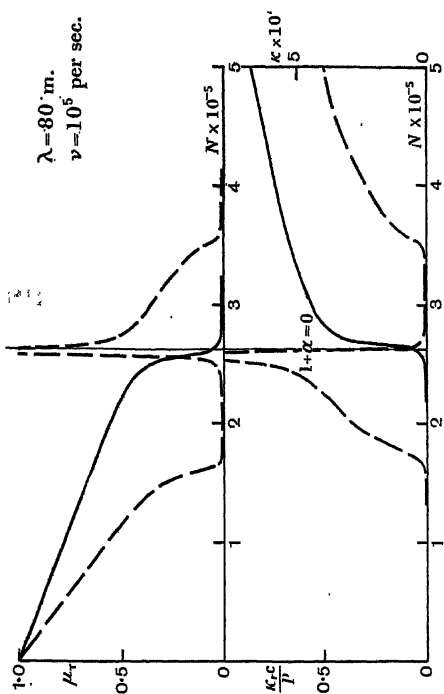


Figure 3.11.

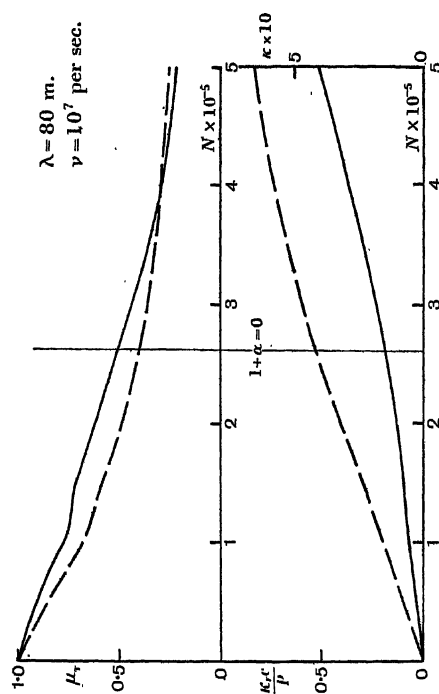


Figure 3.13.

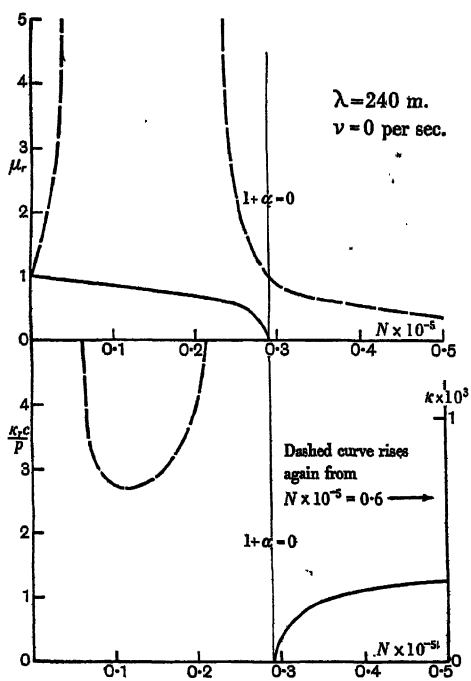


Figure 3.20.

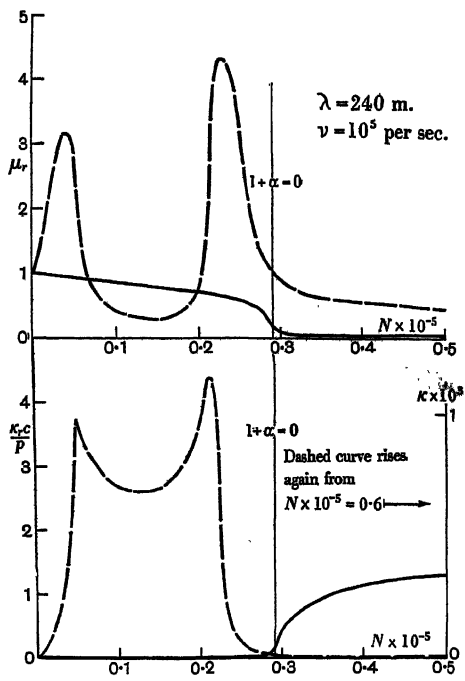


Figure 3.21.

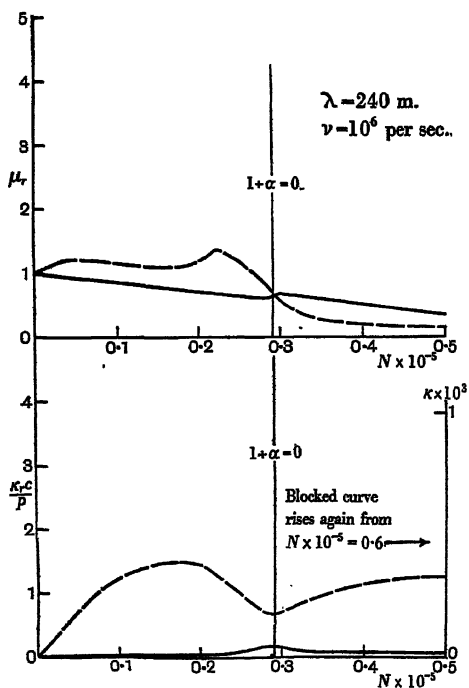


Figure 3.22.

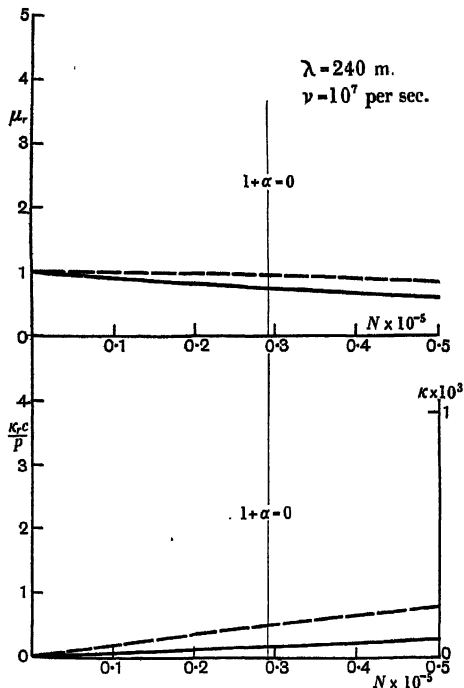


Figure 3.23.

Figure 3.2. Values of μ_r , $\kappa_r c/p$ and κ_r when $\lambda = 240 \text{ m.}$; $\nu = 0, 10^5, 10^6, 10^7 \text{ per sec.}$

$r = a$ ——— $r = b$ - - -

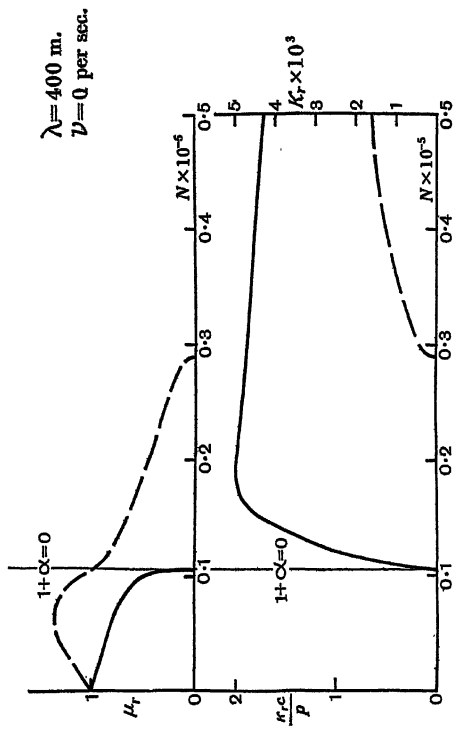


Figure 3.30.

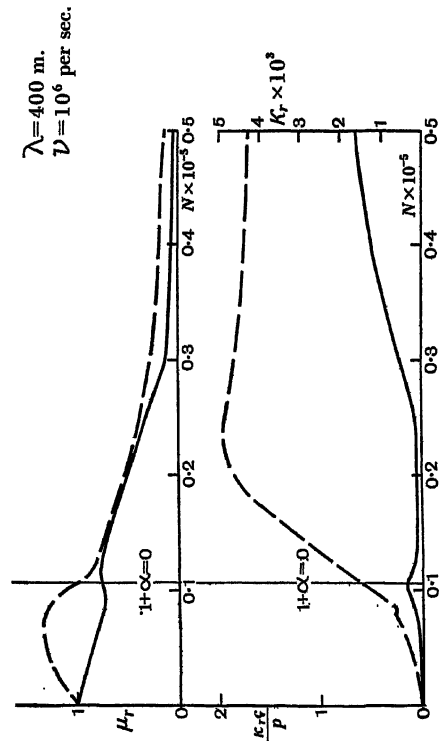


Figure 3.32.

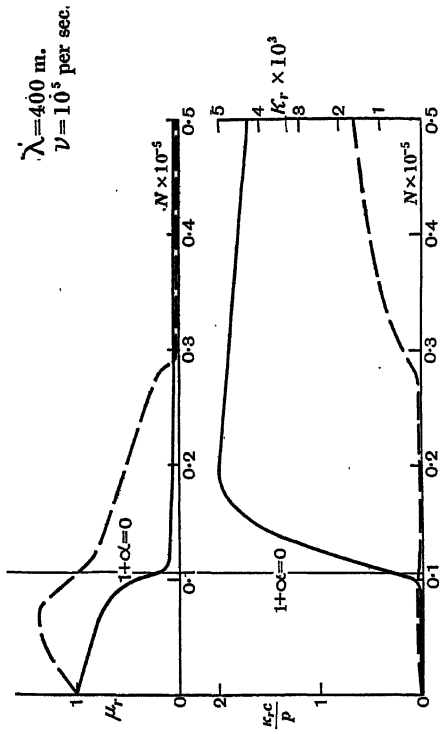


Figure 3.31.

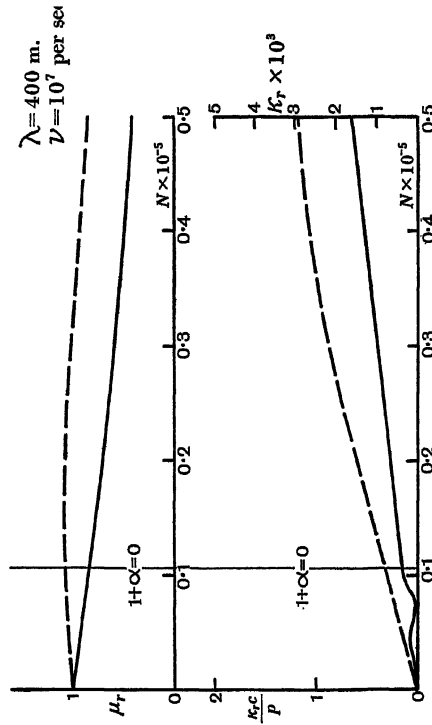


Figure 3.33.

Figure 3.3. Values of μ_r , $\kappa_r c/p$ and κ_r when $\lambda = 400$ m., $\nu = 0, 10^5, 10^6, 10^7$ per sec.

$r=a$ ——— $r=b$ - - - - -

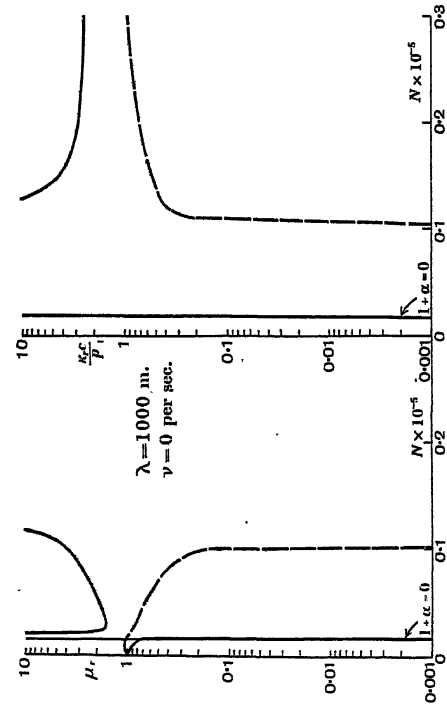


Figure 3'40.

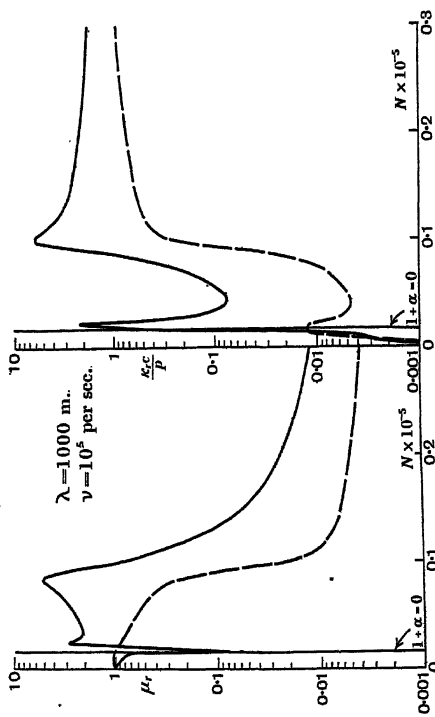


Figure 3'41.

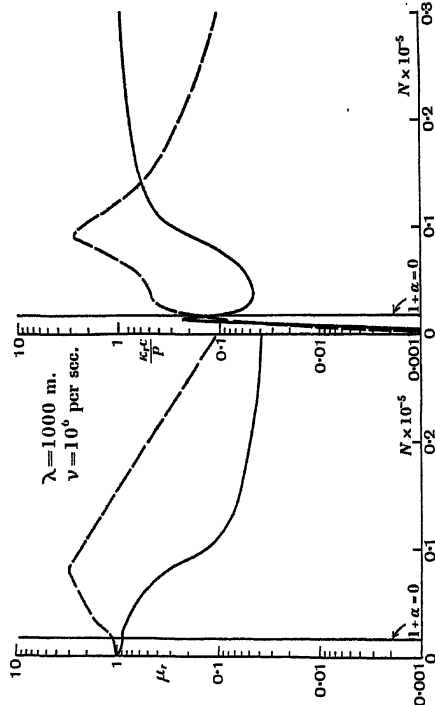


Figure 3'42.

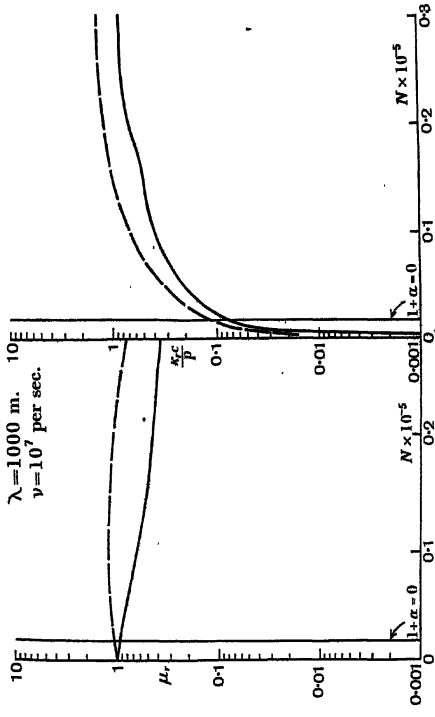


Figure 3'43.

Figure 3'4. Values of μ_r and κ_c/p when $\lambda = 1000$ m.; $\nu = 0, 10^5, 10^6, 10^7$ per sec.

$r=a$ ——— $r=b$ - - -

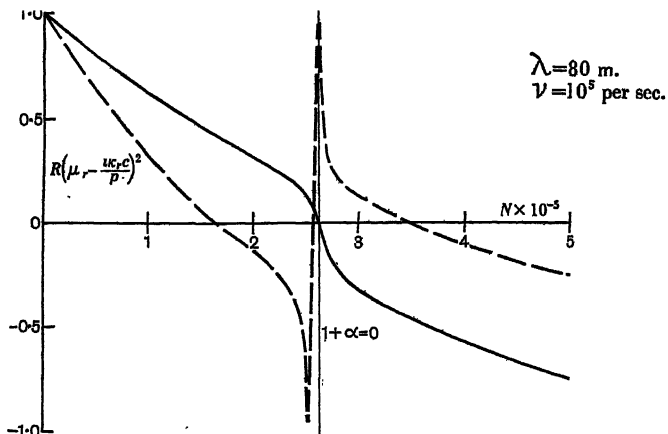


Figure 4.11.

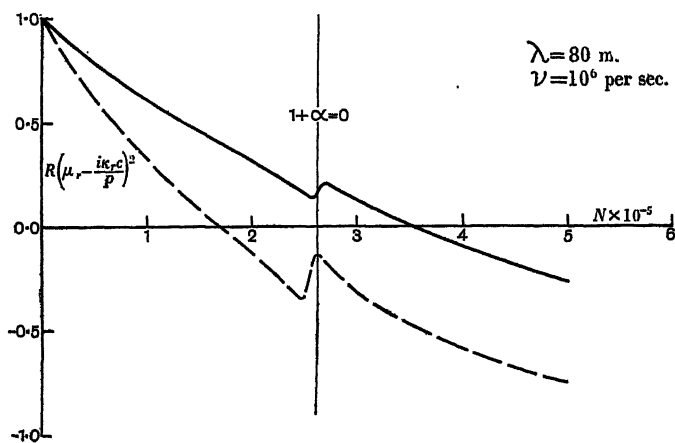


Figure 4.12.

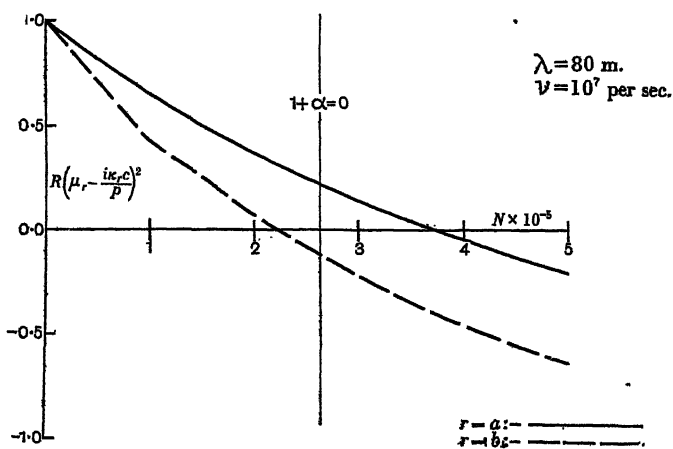


Figure 4.13.

Figure 4.1. Values of $R(\mu_r - i\kappa_r c/p)^2$ when $\lambda = 80 \text{ m.}$; $\nu = 10^5, 10^6, 10^7$, per sec.

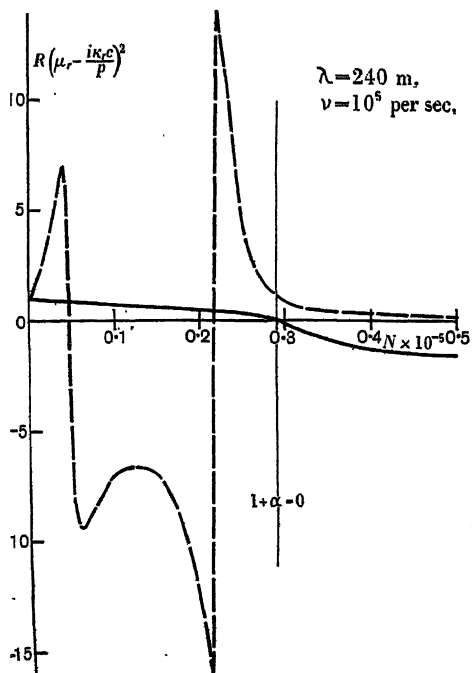


Figure 4:21.

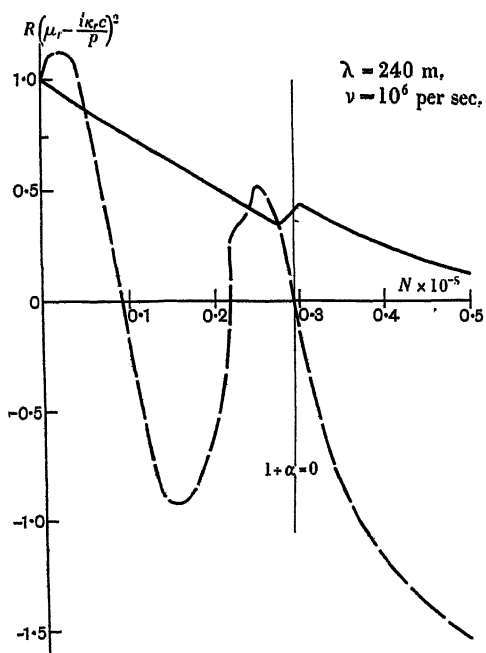


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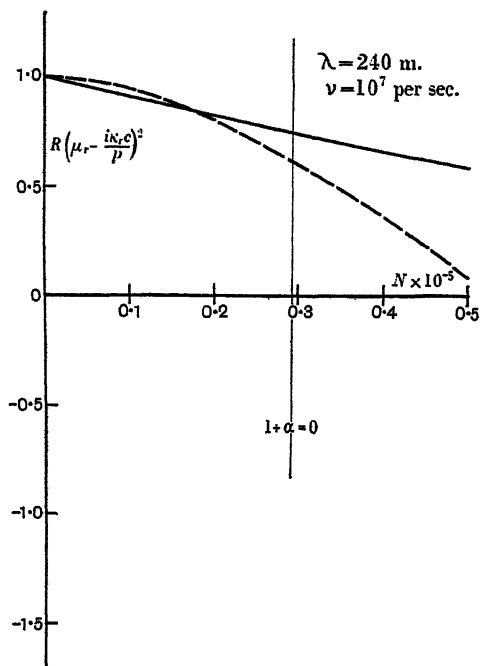


Figure 4:23.

Figure 4:2. Values of $R(\mu_r - \frac{i\kappa_r c}{p})^2$ when $\lambda = 240$ m.; $\nu = 10^5, 10^6, 10^7$ per sec.

$r=a$ ——— $r=b$ - - - -

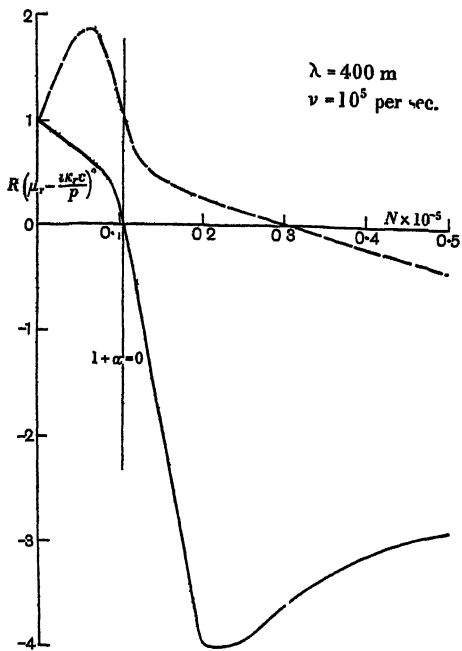


Figure 4-31.

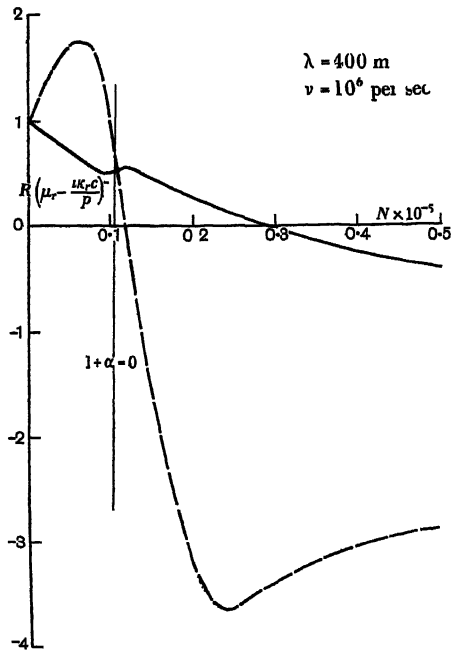


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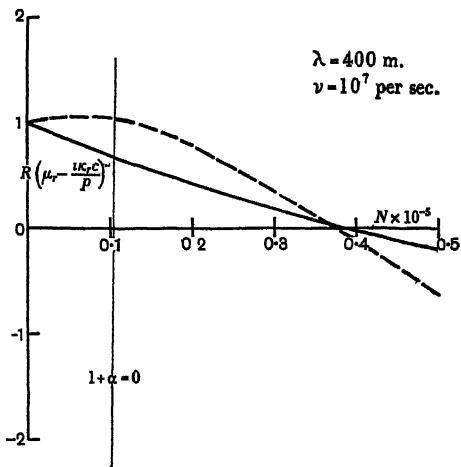


Figure 4-33.

Figure 4 3. Values of $R(\mu_r - i\kappa_r c/p)^2$ when $\lambda = 400 \text{ m.}$; $\nu = 10^5, 10^6, 10^7 \text{ per sec.}$

$r=a$ ——— $r=b$ - - -

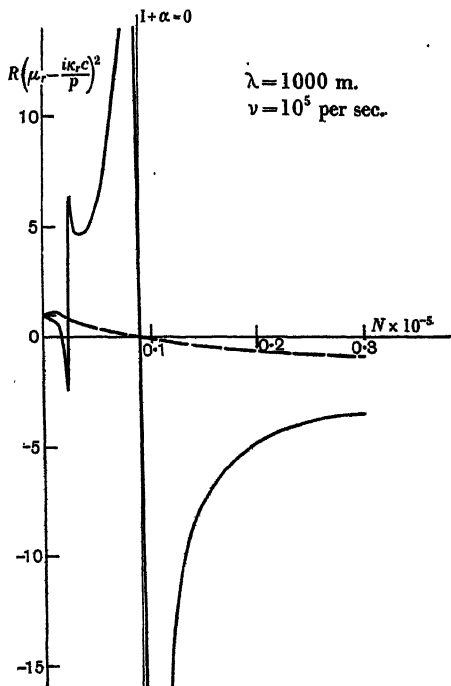


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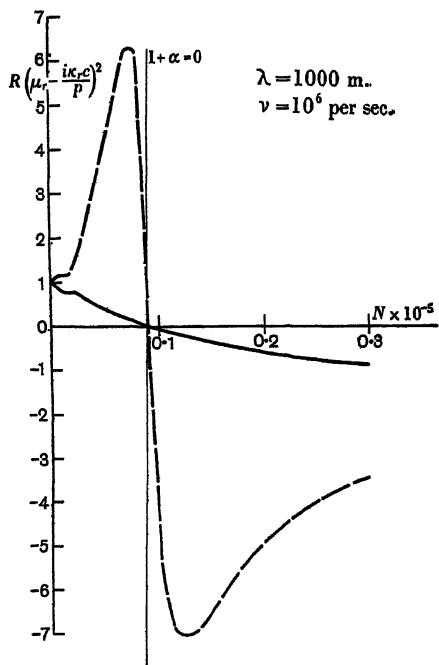


Figure 4.42.

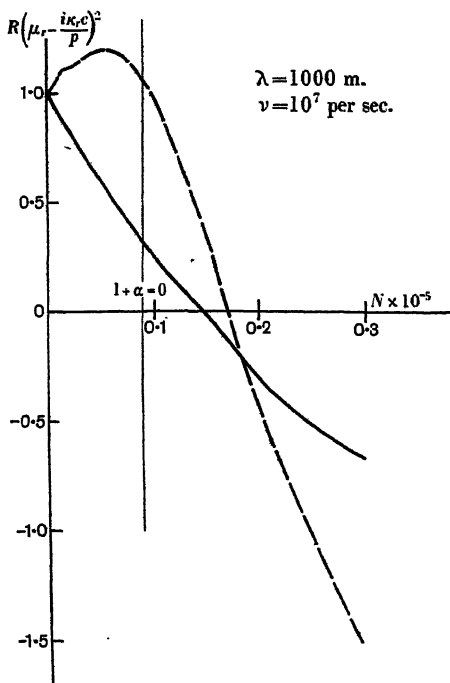


Figure 4.43.

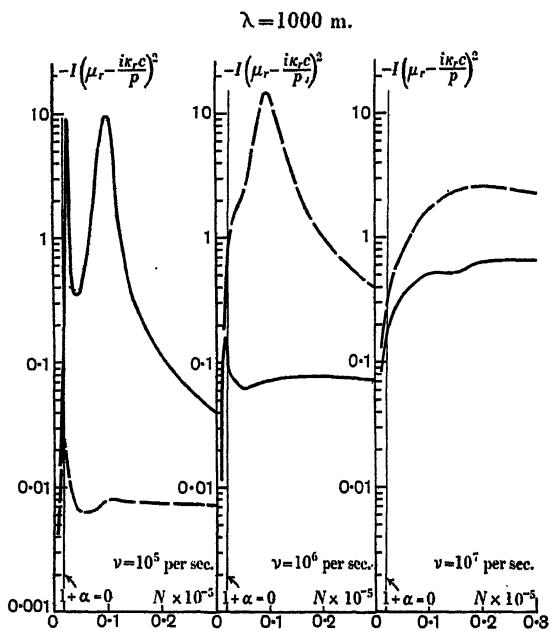


Figure 5.41.

Figure 5.42.

Figure 5.43.

Figure 4.4. Values of $R(\mu_r - i\kappa_r c/p)^2$ when $\lambda = 1000$ m.; $\nu = 10^5, 10^6, 10^7$ per sec.

Figure 5.4. Value of $I(\mu_r - i\kappa_r c/p)^2$ when $\lambda = 1000$ m.; $\nu = 10^5, 10^6, 10^7$ per sec.

$r = a$ ———

$r = b$ - - -

$\lambda = 80 \text{ m.}$

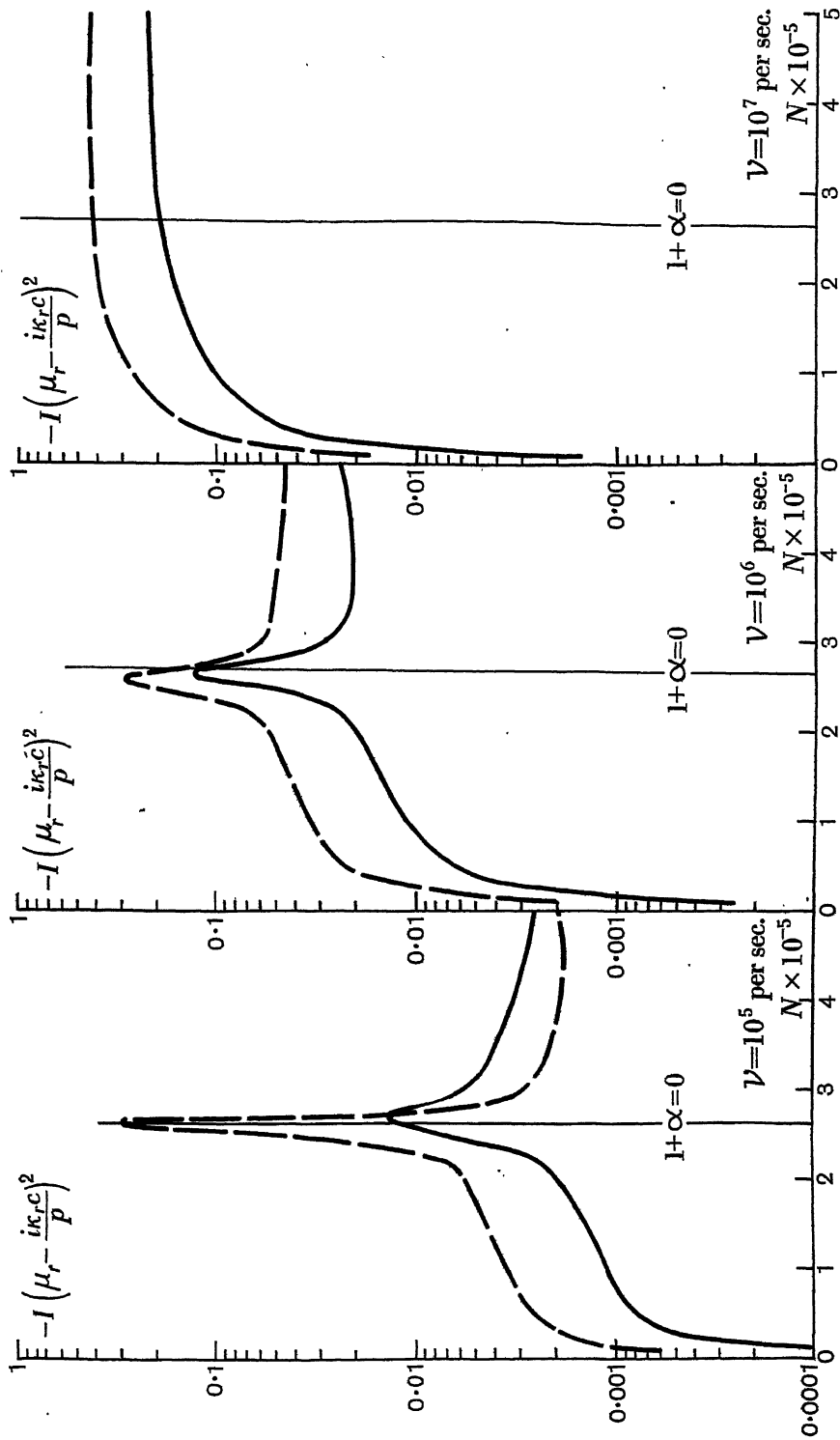


Figure 5.11.

Figure 5.12.

Figure 5.13.

Figure 5.1. Values of $-I(\mu_r - i\kappa_r c/p)^2$ when $\lambda = 80 \text{ m.}$; $\nu = 10^5, 10^6, 10^7$ per sec.

$\tau = a$ ——— $\tau = b$ - - - -

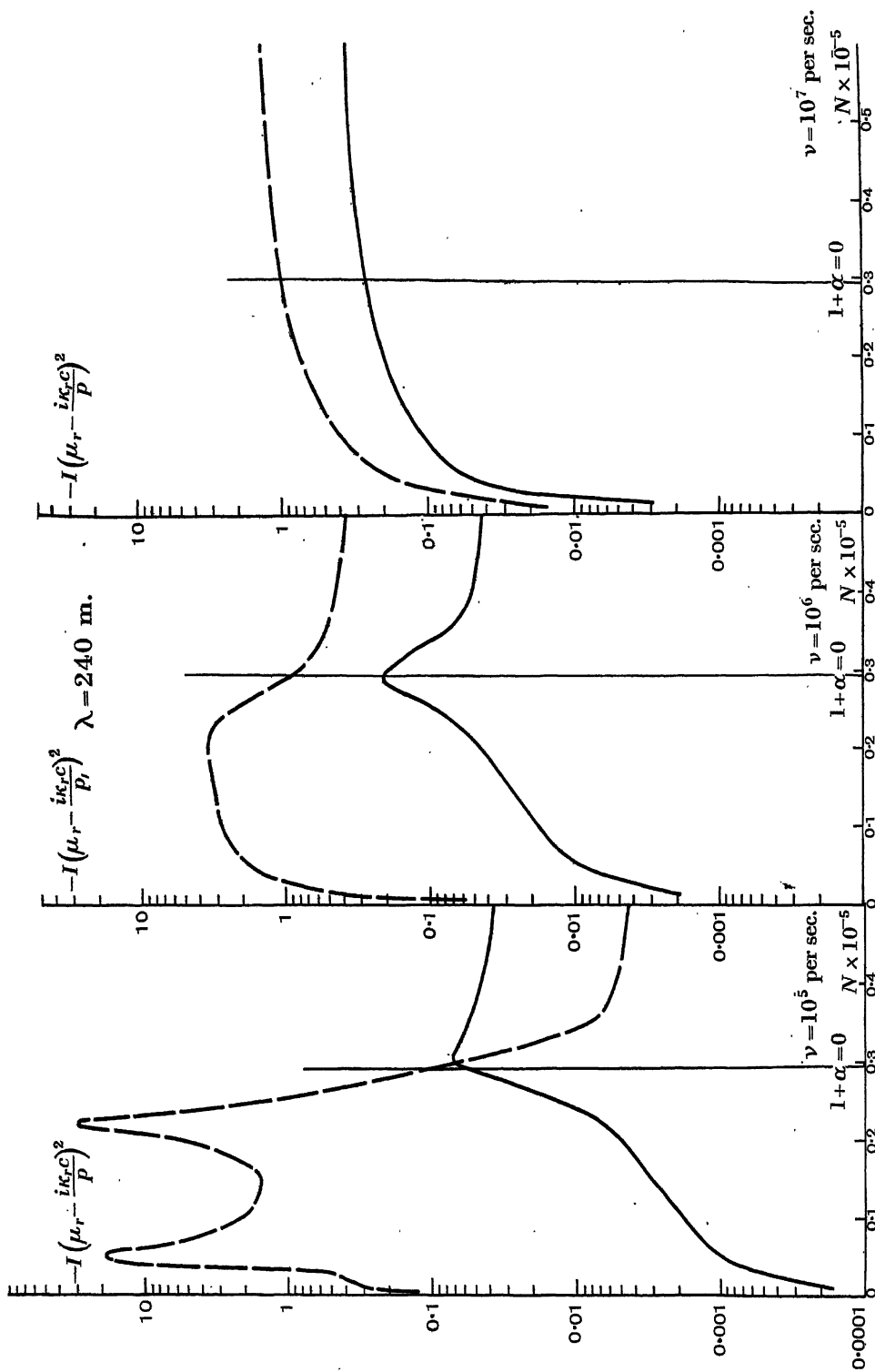


Figure 5'21.

Figure 5'22.

Figure 5'23.

Figure 5'2. Values of $-I\left(\mu_r - \frac{i\kappa_r c}{p}\right)^2$ when $\lambda = 240$ m.; $\nu = 10^5, 10^6, 10^7$ per sec.

$\lambda = 400 \text{ m.}$

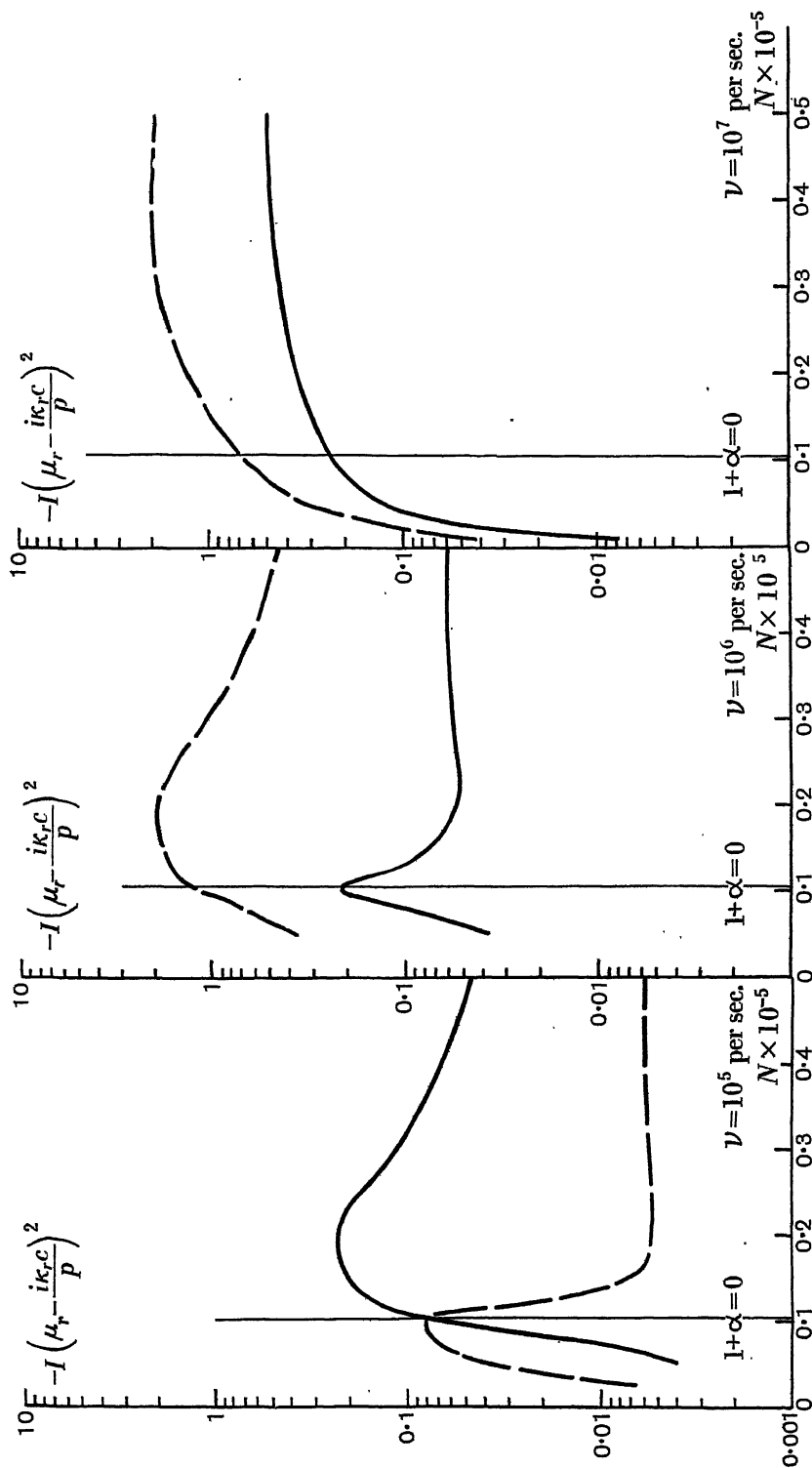


Figure 5'31.

Figure 5'32.

Figure 5'33.

Figure 5'3. Values of $-I(\mu_r - ik_r c/p)^2$ when $\lambda = 400 \text{ m.}$; $\nu = 10^5, 10^6, 10^7$ per sec.

$r=a$ ——— $r=b$ - - - -

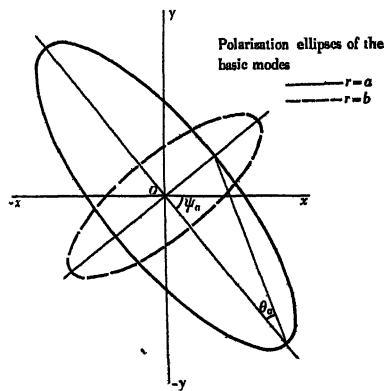


Figure 6.

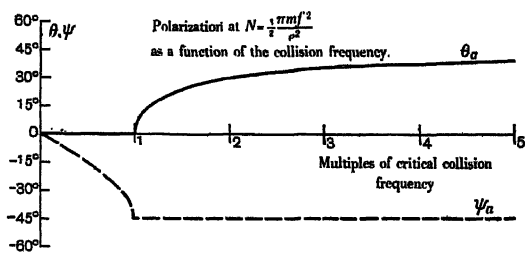


Figure 7.

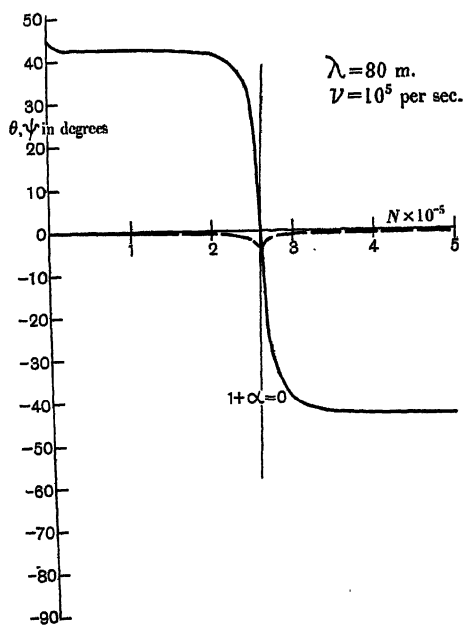


Figure 6.11.

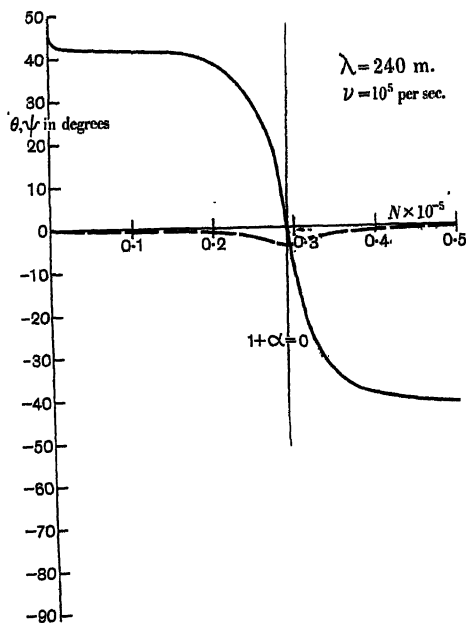


Figure 6.21.

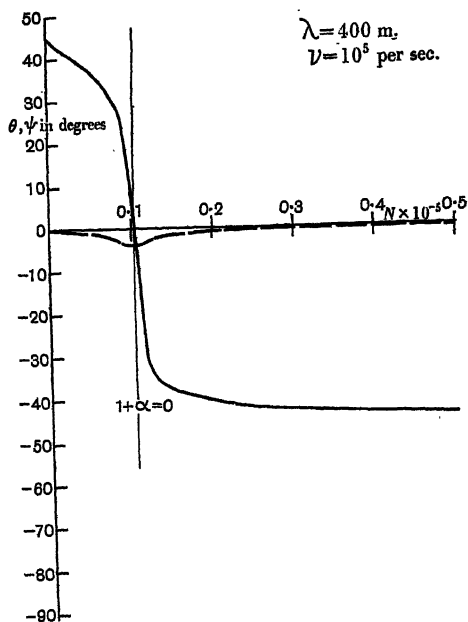


Figure 6.31.

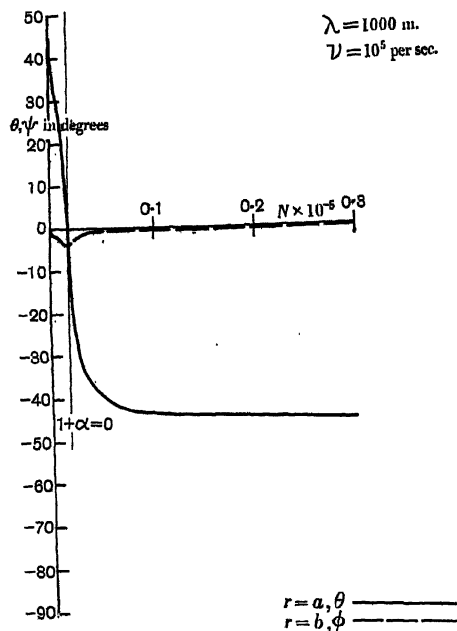


Figure 6.41.

Figure 6.11. Values of θ and ϕ when $\lambda = 80 \text{ m.}$

6.21.	"	"	"	"	$\lambda = 240 \text{ m.}$	} $\nu = 10^5 \text{ per sec.}$
6.31.	"	"	"	"	$\lambda = 400 \text{ m.}$	
6.41.	"	"	"	"	$\lambda = 1000 \text{ m.}$	

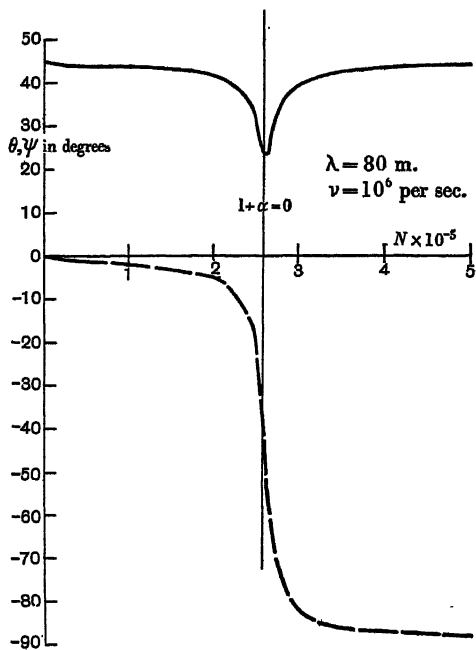


Figure 6.12.

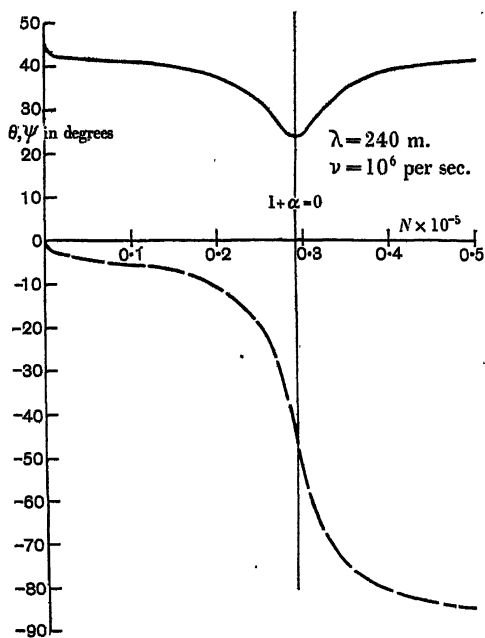


Figure 6.22.

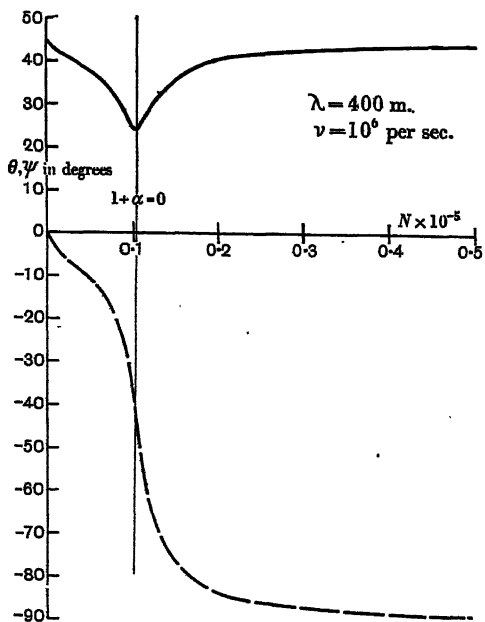


Figure 6.32.

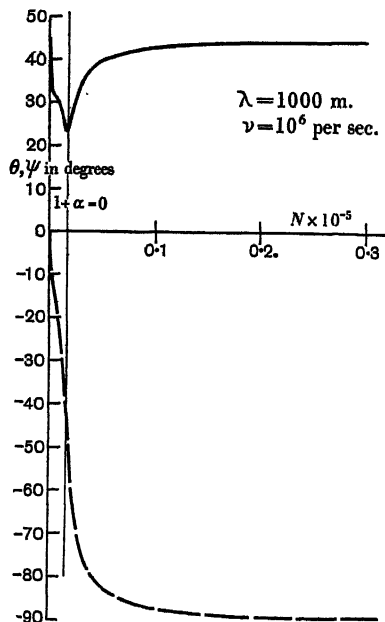


Figure 6.42.

Figure 6.12. Values of θ and ϕ when $\lambda = 80 \text{ m.}$
 6.22. " " " " $\lambda = 240 \text{ m.}$
 6.32. " " " " $\lambda = 400 \text{ m.}$
 6.42. " " " " $\lambda = 1000 \text{ m.}$
 $\nu = 10^6 \text{ per sec.}$
 $r = a, \theta$ ——— $r = b, \phi$ - - - -

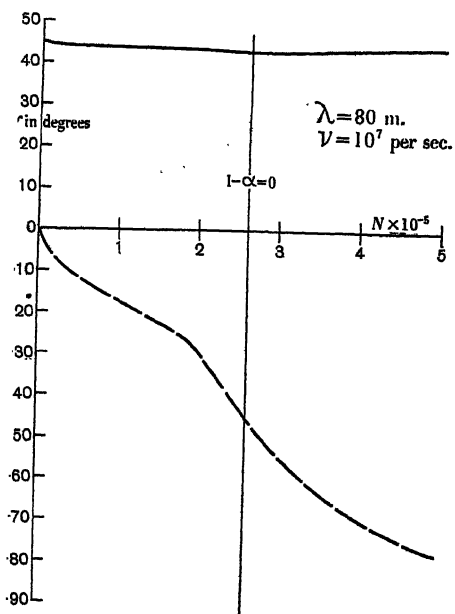


Figure 6.13.

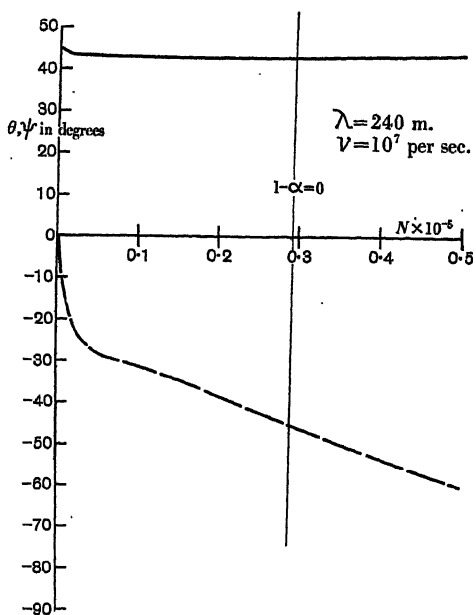


Figure 6.23

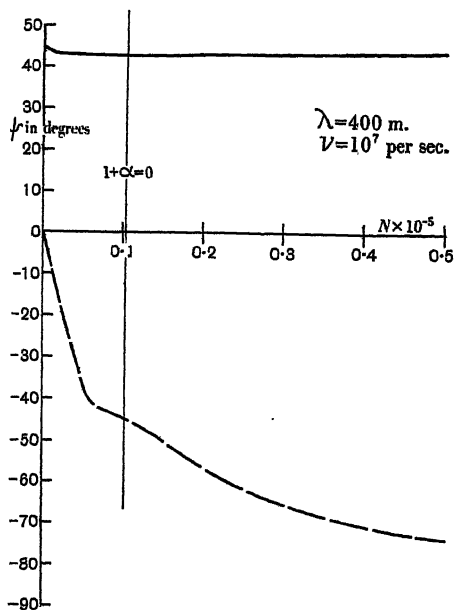


Figure 6.33.

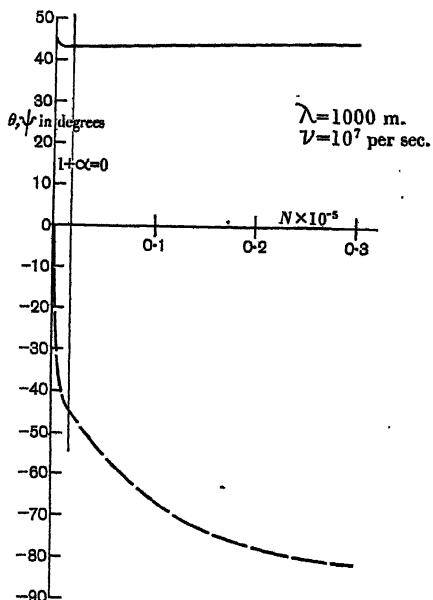


Figure 6.43.

Figure 6.13. Values of θ and ψ when $\lambda = 80 \text{ m.}$
 6.23. " " " " $\lambda = 240 \text{ m.}$
 6.33. " " " " $\lambda = 400 \text{ m.}$
 6.43. " " " " $\lambda = 1000 \text{ m.}$

$V = 10^7 \text{ per sec.}$

$r=a, \theta$ ——— $r=b, \phi$ - - -

THE EFFECTIVE ROTATION TEMPERATURE OF THE NEGATIVE GLOW IN NITROGEN

BY N. THOMPSON, B.Sc., Physics Department, The University, Sheffield

Communicated by Prof. S. R. Milner, December 12, 1933. Read March 16, 1934.

ABSTRACT. The effective rotation temperature has been determined from the intensity distribution in the (0, 0) band of the nitrogen negative system under varying conditions of excitation. The specially designed discharge tubes used for exciting the spectrum are described and the method of calculating the results explained. These results show that the effective temperature increases slightly with the pressure and current-strength, and to a much greater extent with the temperature of the furnace surrounding the discharge tube. At high temperatures it becomes less than the temperature of the furnace, and an explanation of this surprising behaviour is sought. It is concluded that, in this particular case at least, the effective temperature is not identical with the gas temperature though it depends in part on this quantity; it depends also on other factors not yet accounted for in the theory.

§ 1. INTRODUCTION

IT is well known that from the rotational-intensity-distribution in a band spectrum a value for the temperature of the source of the radiation can be deduced even in cases where thermal equilibrium would not be expected, as, for example, in a gas discharge at low pressures. Very diverse values, ranging from 360 to 5000° K. have been found for this effective temperature τ in different gases and with different methods of excitation*. In particular, the so-called nitrogen negative bands have received a considerable amount of attention in this connexion, and even in this one case τ varies over a range from 380 to 1000° K., depending on the conditions of excitation†. There does not appear to have been, however, any systematic enquiry into the effect on τ of these conditions, and in fact the precise significance of that quantity itself is a little vague. The experiments about to be described represent an attempt to throw some light on the second of these questions by investigating the first.

§ 2. EXPERIMENTAL

The measurements were made on the (0, 0) nitrogen negative band at 3914 Å., the spectrum being photographed in the first order of a ten-foot Rowland grating. The density marks for calibrating the plates were obtained by using a step slit on the grating itself; the normal astigmatism of the Rowland mounting was corrected

* J. C. McLennan and others, *Proc. R.S.* 116, 277 (1927). These results are approximate only, since the quantities given as "intensities" are really photographic densities. W. Lochte-Holtgreven, *Z. f. Phys.* 64, 443 (1930); 67, 590 (1931). R. C. Johnson and R. C. Turner, *Proc. R.S. A* 142, 574 (1933).

† W. R. Van Wijk, *Proc. Amst.* 32, 1243 (1929); *Z. f. Phys.* 59, 313 (1930). L. S. Ornstein and W. R. Van Wijk, *Z. f. Phys.* 49, 315 (1928). A. E. Lindh, *Z. f. Phys.* 67, 67 (1931).

by means of a convergent cylindrical lens, placed between the slit and the grating, in such a position that the second focal line from the grating, which gives a stigmatic image and which normally lies behind the photographic plate, was brought into focus. The photographs were photometered on a recording microphotometer of the Moll type. A calculation showed that the instrument width of a line in the spectrum was much greater than the natural width, and therefore that peak intensities could be used instead of the theoretically more accurate integrated area intensities. This conclusion was checked by determining both quantities in one or two cases. The peak intensities were found in the usual way, and the areas with the aid of a device already described*. The ratio of the one to the other was found to be constant except for the first three or four lines of the *R* branch, which were not resolved from lines at the end of the *P* branch, and hence were not used in the final measurements. Only the lines as far as *R* (21) could be measured, since *R* (22) is masked by the head of the (1, 1) band. No results at all were obtained from the *P* branch, since this forms the head of the band, and the resolution was insufficient for intensity measurements.

Two different types of discharge tube were used for the excitation of the bands. The first is shown diagrammatically in figure 1. The tube *A* itself was of steel, and into this slipped a lining tube *B* made of hard glass. This covered the whole of the interior surface of the steel tube with the exception of the conical part *C*. Into this was pushed a truncated cone of brass gauze, the two together forming the cathode, which was earthed. The anode was a ring of copper wire *D* in the annular space at the bottom of the tube. In this manner the usual hollow-cathode method of producing the bands was retained, giving a considerable intensity of light. The positive column was confined almost entirely to the annular space, and the second positive group of bands, which in part overlaps the negative group, was only very faint. The presence of the brass gauze was of great assistance in producing this result. The arrangement also ensured that the gas that was emitting the light was close to the walls of the tube, which possessed a high thermal conductivity, while the tube was of such a shape and so supported that it could easily be placed in a constant-temperature bath, or in a furnace, as shown in the figure. The anode lead *E* was surrounded by a glass insulating sheath which also served to conduct the inflowing gas down to the bottom of the tube. A continuous flow of gas was maintained through the apparatus while a photograph was being taken, the supply being from a cylinder of commercial nitrogen dried by passing over phosphorus pentoxide. A copper-constantan thermocouple was inserted through the bottom of the furnace as at *F* to determine its temperature, and for some of the observations a second and similar couple was interwoven among the meshes of the gauze forming part of the cathode, as shown.

The second form of tube consisted of a piece of the same steel tubing, mounted horizontally and closed at the ends by glass plates. In this case the tube acted as the anode, and the cathode consisted of a spiral of nickel wire, 1 cm. in diameter

* N. Thompson, *Proc. Phys. Soc.* 45, 441 (1933); but on p. 443, line 5, the two focal lengths, given in error as 50 and 100 cm., should be 25 and 50 cm. respectively.

and 5 cm. long, coaxial with the anode and in the centre of its length. There was in addition along the axis of the cathode a fine platinum wire which was used as a resistance thermometer. The furnace wire was wound directly on the central portion of the tube, and the thermocouple was allowed to lie loose inside. In one form, leads were taken from both ends of the cathode as well as from the middle, so that its resistance could be measured while the discharge was passing and its

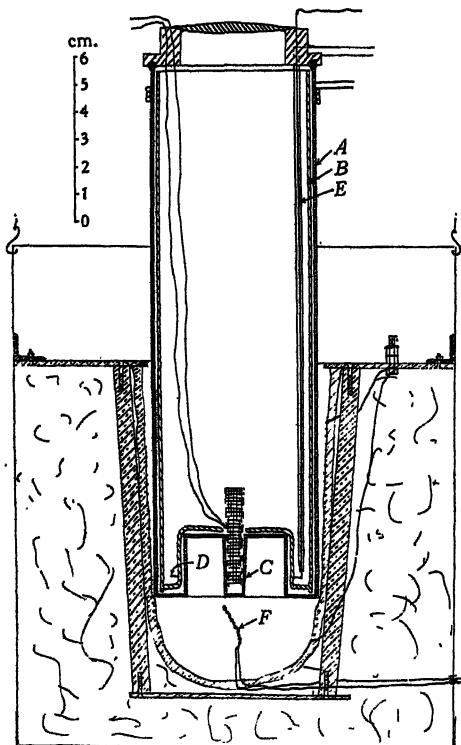


Figure 1. First type of discharge tube; vertical section.

temperature could be determined in this manner. Alternatively, a heating-current could be passed through it and its temperature could thus be varied independently of that of the furnace. The advantage of this second over the previous form of tube was that the region in which the discharge took place was uniformly heated with greater certainty; in addition, the heating was not effected by way of the material of the cathode, and so a suspected source of complications was eliminated.

§ 3. RESULTS

The structure of the bands is very simple, being similar, if we neglect the unresolved fine structure, to that for a $^1\Sigma \rightarrow ^1\Sigma$ transition. The theoretical formula for the intensities in the R branch can in this case be shown to be*

$$I_{R(K)} \propto (K+1) \cdot \exp \{-B_0'hc(K+1)(K+2)/k\tau\} \quad \dots\dots(1),$$

* W. Jevons, *Report on Band Spectra of Diatomic Molecules* (Phys. Soc. 1932).

where $I_{R(K)}$ is the intensity of the K th line of the R branch, K the rotation quantum number, B_0' the rotation constant for the upper $v' = 0$ level, and h , c and k have their usual significance. This expression neglects the variation of ν^4 in the small range covered by one band, where ν is the frequency of line*. Thus by plotting $\log I_{R(K)}/(K+1)$ against $(K+1)(K+2)$, we obtain a straight line with a slope inversely proportional to τ . Using the value 2.07 of B_0' as given by Jevons, and the value 0.69 for k/hc , we can calculate τ . Since the band shows the phenomenon of alternating intensities, each photograph can be made to give two values of τ by treating separately the strong and the weak lines. The line of closest fit was in each case estimated only, the number of points being insufficient to justify the use of

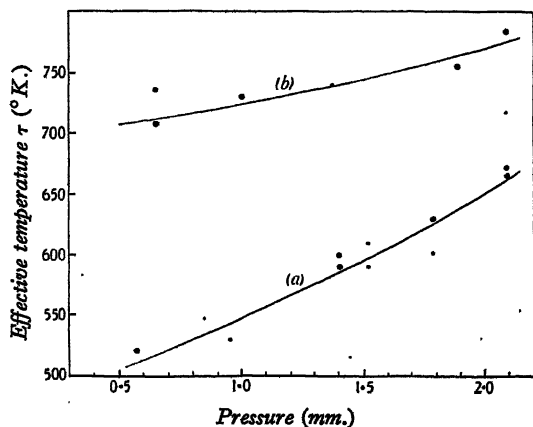


Figure 2.

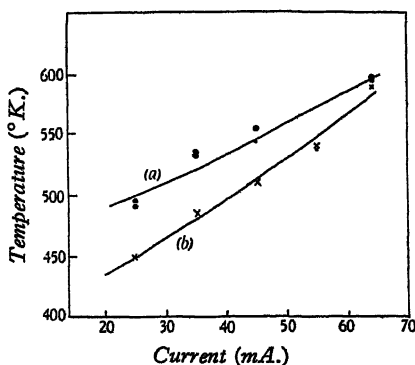


Figure 3.

Figure 2. Showing the effect of varying pressure on the effective rotation temperature; first tube. (a) With the tube at room-temperature; current 31 mA., potential between 424 and 487 V. (b) With the furnace-temperature equal to 650° K.; current 31 mA., potential between 386 and 450 V.

Figure 3. Showing the effect of varying current; first tube. Tube at room-temperature; pressure 0.72 ± 0.02 mm., potential increasing with the current from 386 to 446 V. (a) Effective rotation temperature. (b) Temperature given by thermocouple on cathode surface.

more elaborate methods. The accuracy varied greatly with the quality of the negative. A good result could be trusted to 2° or 3° K., while a photograph unevenly fogged or slightly scratched might give two values of τ differing by as much as 60° K. In the graphs reproduced herewith the size of the experimental point is intended as a rough indication of the reliability of the result, as judged by the deviations from the straight line in the original plot.

As a working hypothesis it was assumed that the following factors might conceivably affect the value of τ : (1) the shape, size, nature and relative position of the electrodes; (2) the pressure p of the gas; (3) the potential drop V across, and the current C through the tube; (4) the temperature of the gas. The first factor was eliminated by keeping the conditions in question constant in any one group of

* The error introduced by this approximation is of the order of 1 per cent of the values of τ and so does not affect the general conclusions.

results. With each type of tube they varied only slightly throughout the whole of the observations, and the different groups of results are, in fact, found to agree well amongst themselves. Moreover, the general conclusions are the same for both types of tube, the differences being small compared to the variations due to the other factors. Considering the vastly different design of the two tubes, we may say that the first factor produces only comparatively small variations in τ .

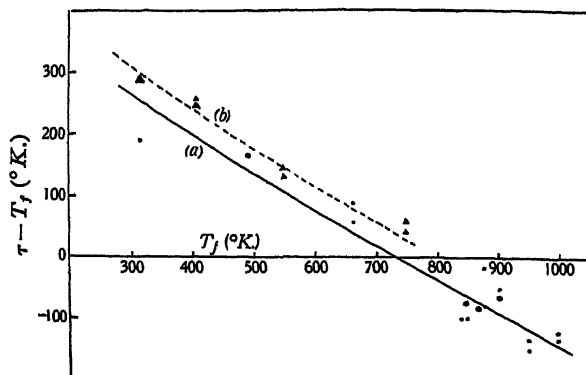


Figure 4. Showing the effect of varying furnace-temperature; first tube. Current 30 mA.; (a) pressure 0.64 ± 0.02 mm., potential between 378 and 412 V.; (b) pressure 1.90 ± 0.02 mm., potential between 406 and 436 V.

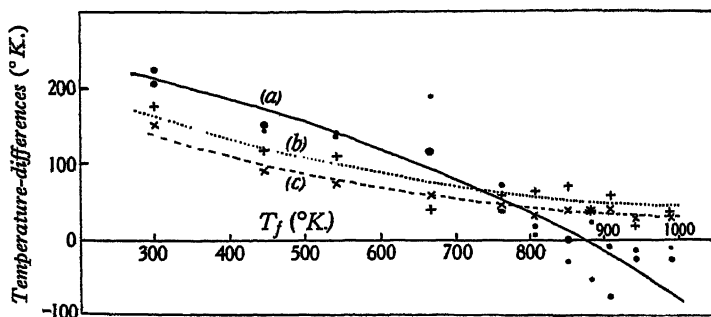


Figure 5. Showing the effect of varying furnace-temperature; second tube. Current 15 mA.; pressure varied, but density of gas approximately constant; potential between 301 and 351 V. (a) Effective rotation temperature, $\tau - T_f$; (b) temperature of cathode, $T_c - T_f$; (c) temperature given by resistance thermometer in negative glow, $\theta - T_f$.

The effect on τ of the other factors was found by varying each of them in turn, while maintaining the rest as far as possible constant. This could not be done exactly, since the variables are not independent: the temperature, pressure and current being fixed, the potential is determinate. Consequently, the first named three were treated as independent variables, and the value of the potential was noted in each case. Only a representative selection of all the results obtained is given here. Figure 2 shows that the effect of increasing the gas-pressure was to raise the value of τ , while figure 3 indicates that the same effect was produced by increasing the

current. These phenomena occurred whether the tube was surrounded by a water bath at room-temperature or heated in the furnace. Several series of results were obtained to show the effect of increasing the furnace-temperature, but one only for each type of tube is quoted, figures 4 and 5. To save space, the results are plotted to show the excess of the temperatures above that, T_f , of the furnace. In all cases τ increased with the furnace-temperature but at a lesser rate, becoming the smaller of the two at sufficiently high values. This holds both when the pressure, figure 4, and when the density, figure 5, of the gas is kept constant. Essentially similar curves were obtained with other constant pressures and currents, and with both types of tube. The temperature of the cathode increased with T_f but always remained the larger of the two, while the temperature indicated by the platinum resistance thermometer in the second tube was correlated with the cathode-temperature rather than with the effective rotation temperature or with the furnace-temperature, and was always slightly the smaller of the two.

§ 4. DISCUSSION

Considering first the temperature T_c of the cathode, we find that its behaviour is quite understandable. The cathode will be at the temperature of the furnace before the discharge is started, and subsequently it will be further heated by bombardment when a current flows. This is in agreement with the known fact that most of the energy input in a discharge tube is dissipated as heat at the cathode. It also accords with the increase in T_c with the current, recorded in figure 3 *b*. It is, moreover, to be expected that, with the second type of tube, the difference $(T_c - T_f)$ will become less as T_f increases. For if the heat were lost solely by radiation to the walls, the equation

$$a(T_c^4 - T_f^4) = \text{constant (energy input)}$$

would hold, while if the dissipation were solely by conduction along the leads, we should have

$$b(T_c - 300) = \text{constant},$$

300° K. being approximately the temperature of the cold end of the leads. Actually something between these two extremes will hold, and the shape of the curve 5*b* is in agreement with this scheme.

Turning to the temperature θ of the platinum filament, we note that had the latter been totally enclosed by the cathode we should have expected θ to be equal to T_c . In practice, radiation losses through the interstices of the cathode, and conduction along the filament leads, will both tend to make θ less than T_c , so that the general form of the relation is again explained. Thus it may be stated with a fair degree of certainty that the measured values of T_c and θ represent the real temperatures of the cathode and filament respectively. Consequently, in so far as a gas which is in neither thermal nor mechanical equilibrium can be said to have a temperature, that of the gas in the negative glow probably lies between the fairly narrow limits given by T_c and θ .

What, then, is the significance of the quantity τ ? Whether or not the conclusions of the last paragraph are accepted, τ is obviously not the gas-temperature, since it is most unlikely that this magnitude will be actually reduced by starting the discharge, and τ has been shown to be not only less than T_g but even less than T_f . Although it is not equal to the gas-temperature, its variation when the furnace is heated shows that it depends in part on this quantity. It is also probable that the increase in τ with increasing current is due indirectly to this same cause, since the increased cathode-temperature (see figure 3 *b*) will cause an increase in the gas-temperature in its neighbourhood. This view is supported by some further experiments with the second tube, in which a heating-current through the cathode raised both θ and τ , the increase being almost as much as when the cathode was raised to the same temperature by heating the furnace. The (τ, θ) relations for the two cases were very closely similar, but strict comparison is not possible since the conditions of pressure and current were not the same in the two cases. No such simple explanation is obvious to account for the variation of τ with the pressure, and the physical mechanism of this, as of the major problem of the divergence of τ from the gas-temperature, remains obscure.

In conclusion, it is of interest to consider the bearing of these results on the question of the duration of the excited state. They indicate that it is not long enough for the excited molecule to reach temperature equilibrium with its surroundings; for if it was, we should expect τ to be equal to the gas-temperature, i.e. approximately to θ . Thus formula (1), which is based on the assumption that such equilibrium is established, is not strictly valid. Van Wijk, in a recent paper*, has suggested that the life of the excited molecule is so short that the rotational-energy-distribution which existed before the molecule was excited is not appreciably disturbed before it radiates. In the Boltzmann factor in the formula for the intensity-distribution we must then insert the constant for the lower energy-level: if this is taken as being the ground state of the N_2^+ molecule, we obtain instead of (1)

$$I_{R(K)} \propto (K+1) \cdot \exp \{-B_0''hc(K+1)(K+2)/k\tau\} \quad \dots\dots(2)$$

where B_0'' is the rotation constant for this state. The effect of this change on our results is to reduce all the values of τ by about 7.5 per cent. If on the other hand we assume that the excited N_2^+ ion is formed direct from the ground state of the neutral molecule N_2 , and if, following Van Wijk, we postulate that there is no change in the rotation quantum number when this takes place, B_0'' must take the value for the ground state of the neutral molecule. This would produce a reduction of about 4 per cent in the values of τ . If Van Wijk's suggestion represented the whole truth, the change should have made τ equal to θ , while, in actual fact, this is not true in either case, and the essential characteristics of the experimental curves remain unaltered and unexplained.

Thus neither alternative holds good, and all that can be said at present is that the rotational-energy-distribution is modified when the molecule is excited. The resulting energy-distribution is approximately of the Boltzmann form, but the

* W. R. Van Wijk, *Z. f. Phys.* 75, 584 (1933).

effective temperature deduced is not identical with the gas-temperature; it can, in different circumstances, be either greater or less than this quantity, and depends on some other factors which have not yet been taken account of in the theory.

§ 5. ACKNOWLEDGMENTS

Finally, I must tender my very best thanks to Dr Milner and his staff in the University of Sheffield for their assistance and encouragement during the progress of the work, and to the Department of Scientific and Industrial Research and the Sheffield Town Trustees for the scholarships which rendered it possible.

DISCUSSION

Mr J. H. AWBERY. The fact that the effective temperature exceeds the furnace-temperature by smaller amounts as the latter is raised, until their relative positions becomes actually reversed, is surprising. Is it possible that this result is due to errors in assessing the furnace-temperature? The latter was measured by means of a copper-constantan couple, an instrument which is not usually found reliable at temperatures of the order of 1000°K. , where oxidation of the copper limb is liable to become serious. Possibly the author could show the calibration of the couple before and after use, and so dispose of this doubt.

AUTHOR'S reply. I was unfortunately not able to recalibrate the thermocouple after use, so it must be admitted that Mr Awbery's suggestion is not altogether impossible. Nevertheless I do not think that it is probable, since the couple, when heated, would be in an atmosphere of almost pure nitrogen. Oxidation may have occurred during the calibration, but then this would be taken account of in the results obtained. Moreover, results consistent within the limits of error were obtained independently of the previous heat treatment of the couple.

THE MEASUREMENT OF FLAME TEMPERATURES IN A PETROL ENGINE BY THE SPECTRAL LINE-REVERSAL METHOD

By S. S. WATTS, B.Sc. (Eng.)

AND

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both of the University of London

Communicated by Dr L. F. Bates, January 19, 1934. Read March 16, 1934.

ABSTRACT. Hitherto no satisfactory method has existed for the measurement of the temperatures which occur during combustion in a petrol engine, but it is shown that the reversal of a spectral line provides a suitable method. It is found that the maximum temperature in the engine cylinder persists for a longer period than the maximum pressure.

§1. INTRODUCTION

ONE of the earliest attempts to measure flame-temperatures was that of F. Kurlbaum*, who compared the temperature of a luminous flame with that of a black body. In the case of a non-luminous flame, Féry† proposed to introduce a suitable metallic salt into the flame and to apply the principle of spectral line-reversal. This was first enunciated by Kirchhoff and the method consisted in obtaining a luminous source at the same temperature as the flame under observation and then measuring the temperature of this source by means of an optical pyrometer. E. Bauer‡ showed that the result was independent of the choice of metallic salt.

This has been confirmed and the method more fully developed in a valuable paper by E. Griffiths and J. H. Awbery§. In that paper many of the possible sources of error have been discussed and in particular the method has been applied to the measurement of the temperature of combustion of carbon monoxide and air in an explosion vessel.

In this communication, the authors have utilized the method for the determination of the flame-temperatures at various points of the working cycle of a petrol engine, these temperatures ranging from 1200° C. to 2200° C. This is a problem which has exercised the minds of engineers for some years and it is felt that the results are not without interest to physicists. Previous experimenters have almost

* *Phys. Z.* 3, 187 (1902).

† C. Féry, *Compt. Rend.* 137, 909 (1903).

‡ *Compt. Rend.* 148, 908 and 1756 (1909). Cf. *Traité de Pyrométrie Optique* by G. Ribaud. pp. 415, 416 (1931).

§ *Proc. R.S. A* 123, 401 (1929).

invariably made use of thermocouples; these have inherent disadvantages, such as time lag and, in the case of very small and unprotected couples, instability of calibration*. A further difficulty in the use of thermocouples is that in an engine they are subjected to violent explosion waves, which cause mechanical breakage, even when the maximum explosion temperature is reduced below the fusing point of the couple by diluting the explosive mixture present. The highest temperature so far recorded in a gas engine was computed solely from the fact that the end of the couple had just fused†. Other experimenters‡ on gas engines have used resistance thermometers, but these again could not be employed at the highest working temperatures. Since the commencement of these tests, it has, however, come to the authors' notice that a couple, which is said to be satisfactory up to a temperature of 2000° C.§ has been devised.

§2. APPARATUS

As a full description of the principles involved is given in the paper of Griffiths and Awbery||, the present authors will limit themselves to describing the apparatus used in their own tests.

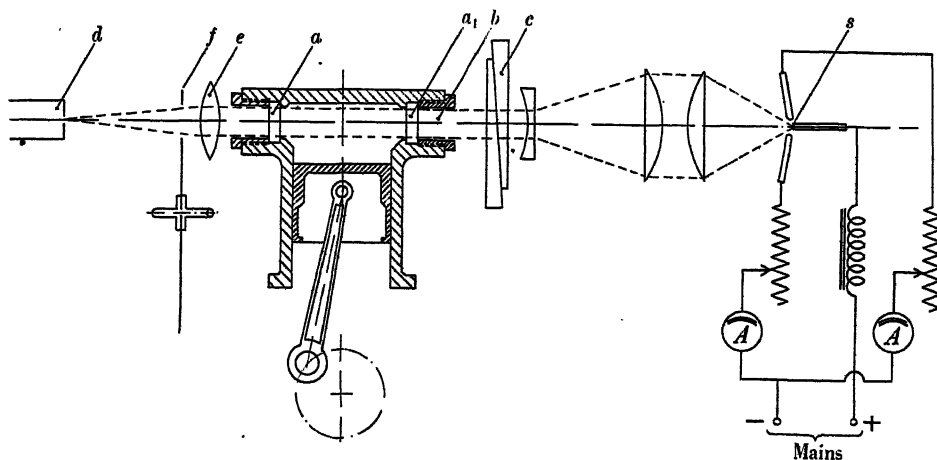


Figure 1. *a, a₁*, quartz windows; *b*, parallel beam; *c*, neutral wedges; *d*, spectroscope; *e*, lens; *f*, stroboscopic disc; *s*, source of light.

In figure 1, *a* and *a₁* represent two quartz windows let into the combustion space of an engine cylinder designed specially to receive them. Light from a source *s* passes through a combination of lenses and emerges as a parallel beam at *b*, the intensity being controlled by a pair of adjustable neutral wedges at *c*. After passing through the engine cylinder, this beam is focused on to the slit of a spectroscope *d* by means of the lens *e*. Between this lens and the spectroscope is arranged the

* Cf. "Pyrometric Practice," *Bureau of Standards Tech. Papers*, 170, 23 (1921).

† E. Coker and W. A. Scoble, *Proc. Inst. C.E.* 196, 1 (1914).

‡ H. Callendar and W. E. Dalby, *Proc. R.S. A* 80, 57 (1908).

§ O. Feussner, *E.T.Z.* 54, 155 (1933).

|| *Proc. R.S. A* 123, 401 (1919).

stroboscopic disc f which is driven at half the speed of the engine so that light passes to the slit in d once in every working cycle. The disc can be phased to any desired position of the engine-mechanism. The wedges c are adjusted so that reversal of the sodium line occurs while the engine is running. The engine is then stopped and the spectroscope replaced by a monochromatic pyrometer of the disappearing-filament type. In order to obtain a reading on the pyrometer, the left-hand quartz window a and the lens e are removed.

For each point three sets of readings were taken after the conditions of running, such as load, temperature of cooling-water, etc., had become steady. As this necessitated a certain lapse of time while adjustments were made, it was found desirable to use a steady source of light at s . A standard Pointolite lamp, although it acted as a constant source of light, did not allow wedges of reasonable density to be used, and a serious time lag was introduced if an attempt was made to vary the intensity of light by means of a series resistance in the Pointolite circuit. The authors therefore used an arc lamp provided with one positive and two negative carbons, each 6 mm. in diameter, as described by Forrest* who used this lamp as a standard of illumination.

It was found that reliable readings could be obtained with the engine-crank placed at settings between 5° and 70° later than that with the piston in its uppermost position, known as the "top dead centre." Over this range it was possible to repeat individual readings to within 15° C. Readings taken after this range of settings became less certain since the temperature was then about 1200° C. and the spectrum observed under these conditions approached the limit of visibility. It was possible to improve matters in this respect by an alteration in the lens system or by increasing the size of the aperture in the stroboscopic disc, but it was found inconvenient to work the alternative-lens method as slight alterations in alignment, due to vibration of the engine, were liable to cause errors. Again, an increase in the size of the hole in the disc would make the cyclical position at which temperatures were recorded less definite.

Measurements taken before top dead centre was reached were liable to slight errors, firstly because in this region combustion was not general but very localized, and secondly there were variations between one explosion and another, which are inevitable with this type of engine. It is well known that pressure-measurements in a petrol engine at individual points near the maximum, taken with a Farnboro indicator, also show similar marked variations.

The authors used a Hopkinson optical indicator to obtain photographic records of the (pressure volume) diagrams, as shown in figure 2. The complete data are collected in figure 3, which shows pressure plotted on a base of time or crank-angle, together with the corresponding temperature-readings. The ignition advance for both curves was 20° , which was found to be the best setting for this particular speed (1016 r.p.m.) at full load.

As has been pointed out by Griffiths and Awbery† the method is only valid if

* J. F. Forrest, *Electrician*, 71, 729 (1913).

† *Proc. R.S. A* 123, 401 (1929).

the engine flame is non-luminous. With the petrol used, Pratts No. 2, no continuous spectrum could be observed when the centre of the cylinder-head was focused on the slit of the spectroscope. To reduce any possible error in case of the flame being slightly luminous, the lens system was arranged so that very little light from the gas itself reached the spectroscope; consequently the effect on the continuous spectrum from the arc lamp was negligible.

The amount of sodium normally present in the flame of a petrol engine is insufficient to give really satisfactory reversal. A 1 per cent solution of sodium ethylate in alcohol was therefore added to the petrol in the proportion of 15 cm³ to each gallon. This fluid is combustible and appears to have no measurable effect on the performance of the engine.

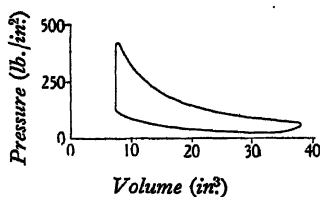


Figure 2.

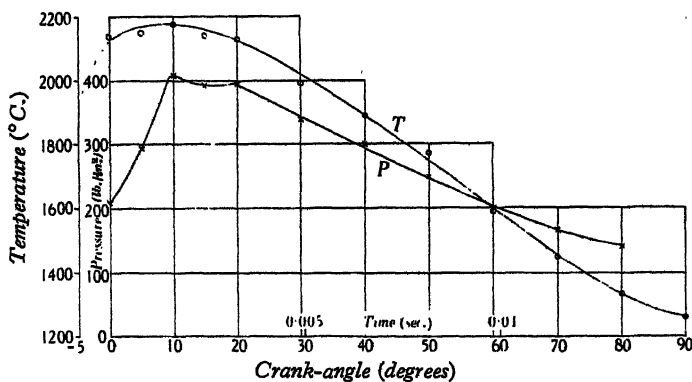


Figure 3. *P*, pressure; *T*, temperature.

§3. RESULTS

It is of interest to note that in figure 3 the period of maximum pressure is of much shorter duration than that of maximum temperature. Probably the explosive mixture burns comparatively slowly so that various parts of the charge in turn rise to the highest temperature, while the pressure still continues to rise until a considerable proportion of the gases has been ignited. There appears to be a limit (possibly due to dissociation) to the highest temperature as has been pointed out by

Tizard and Pye*, who have made a number of calculations of explosion temperatures in which this factor is taken into account. A direct comparison with their calculations cannot be made, however, as they assumed that all the charge was burned instantaneously at the top dead centre. For heptane, for example, with the chemically correct proportion of air, they calculated a maximum temperature of 2590° C.

The present authors consider it unnecessary to include here a more complete analysis of their results which bear on the engineering side of the problem; these will, it is hoped, be reported elsewhere. In conclusion, they wish to point out that this new development of the spectral line-reversal method should prove of considerable value in the investigation of the problems of the internal-combustion engine.

§4. ACKNOWLEDGMENTS

The authors wish to thank Professor E. N. da C. Andrade for the loan of a direct-vision spectroscope and Dr L. F. Bates for many useful suggestions.

DISCUSSION

Lord RAYLEIGH remarked that the use of an arc lamp with one positive and two negative carbons for producing steady illumination had been attributed by the authors to Forrester (1913). It had, however, been adopted as early as 1908 by Sir William Abney at the Imperial College of Science.

Dr L. F. BATES. I was very pleased to be able to communicate this paper, because it describes an interesting and important practical application of some fundamental experiments carried out by two of our most active Fellows, Dr Griffiths and Mr Awbery. I have followed the work which has just been described from its commencement, and I have never ceased to be impressed by the speed and accuracy with which the individual determinations of the temperature of the gas at any instant can be made. It will have been noted that these individual readings can be repeated to within 15° C. This does not represent the limit of accuracy of the temperature-measurements themselves, but is merely a statement of the fact that the working conditions of the petrol engine vary to this extent, for obviously the supply of petrol etc. cannot be strictly controlled. I may add that considerable interest is being taken in these measurements by engineers. Only a few days ago a foreign engineer, reading a paper before a London institute, stated that there was no method of measuring the temperature inside the cylinder of a petrol engine with any degree of accuracy. I hope that the advance proof of this paper will give him satisfaction.

Dr EZER GRIFFITHS. The authors' method of selecting the point at which readings are to be taken is simple and effective. The temperature measurements are free from time lag, but can the same be said of the pressures?

* *Report Empire Motor Fuels Committee, Inst. Auto. Engrs.* 18, 1 (1923).

Mr J. H. AWBERY. Since the measurements made on this engine include simultaneous determinations of the pressure p , the temperature T , and the specific volume v , it is possible to substitute in the equation $pv = nRT$ and so determine n at different points of the cycle. This should throw some light on the questions whether dissociation takes place, and whether after-burning is appreciable. The fact that the flame is radiating cannot be taken as evidence that combustion is still proceeding, and therefore the temperatures alone do not give evidence as to after-burning.

A word of warning may be uttered in connexion with the determination of n in the above equation. The experiments give the average values of p and of v taken through the cylinder at any instant, but the value of T is the maximum. If, for example, the centre of the charge is the hottest part, then it is this temperature that is measured. Thus n may have relative significance—changes of n while the valves are closed would be evidence on the chemical questions involved—but the actual value is not accurately known.

AUTHORS' reply. We have to thank the President for calling our attention to the fact that the three-carbon arc was in use as early as 1908; we also thank Dr Bates for his observations.

With regard to the question of time lag in the pressure-measurements, the Hopkinson indicator used was the best instrument available and should be reasonably accurate at the speed of the engine, 1016 r.p.m. We had not overlooked the suggestions made by Mr J. H. Awbery, and in fact we have already found that pv/T , calculated for a number of points on the expansion stroke, is far from constant. The value increases with time or increase of the volume v behind the piston, and probably implies that combustion is still proceeding.

AN APPARATUS FOR THE DETERMINATION OF THE DEW POINT

By ERIC B. MOSS, B.Sc. (Lond.)

Received January 24, 1934. Read and demonstrated March 16, 1934.

ABSTRACT. The paper describes an optical system which, using diffraction by the dew droplets on a mirror, aids greatly the visual detection of dew formation. Then follows an account of the application of this system to an automatic photoelectric apparatus for maintaining a mirror at the dew point. Results are given of experiments made to find the effect on the accuracy obtainable of the difference between atmospheric temperature and the dew point, and of varying air velocities round the apparatus.

§ 1. INTRODUCTION

THERE are several physical methods of finding the humidity or partial pressure of water vapour in an atmosphere, but the greatest reliance is usually placed on the dew-point determination even though the measurement may call for skill on the operator's part. Suggestions* have been made of arrangements and devices designed to aid the detection of dew and thus to increase the precision of measurement, and the first part of this paper is devoted to the description of an optical system for this purpose.

The eye sees dew on a mirror by reason of light which is diffracted and scattered by it; therefore to secure the greatest sensitivity not only must the mirror be illuminated intensely but also the eye must be shielded from the directly reflected beam so as to be in the most sensitive condition. Such shielding requires the reflected beam to be definite, and the use of an optically worked mirror in the system under discussion ensures this. Further, this system uses the relatively intense diffraction which occurs at small angles to the direct beam. The design is well adapted for use with photoelectric apparatus, which is not called upon to respond to small changes in an intense beam, as it would be if the fall produced in the reflecting-power of the mirror by a dew film were used as the basis of detection. Instead the photoelectric apparatus only has to detect the incidence of light, and thus it can be used at high sensitivity.

§ 2. THE OPTICAL SYSTEM

Recently the author devised a sensitive apparatus for the detection of smoke† and since it depended on diffraction of light by the smoke particles it seemed capable of being adapted to detect dew on a mirror. Alterations were necessary, and the modified optical system is shown in figure 1.

* E. Griffiths, "Discussion on Hygrometry," *Proc. Phys. Soc.* 34, 27 (1921); S. R. Williams, *Rev. Sci. Inst.* 4, 549 (1933).

† British Patent Specification No. 396390.

The mirror *C*, figure 1, is that on which the dew is formed, and in the present apparatus is of stainless steel, optically worked and polished. It is illuminated by a beam from the lamp, concentrated by the condenser *A* which forms an image of the filament near lens *B*. This lens is of wide aperture, and of such a focal length that an image of lens *A* is formed on the stop *D*. Since all light entering the system does so through this lens *A*, stop *D* will intercept that light-reaching lens *B* by direct reflexion. Lens *B* also produces an image of the mirror *C*, but this is larger and beyond the stop *D*, at *E*, and the rays forming it are not obstructed seriously by the stop. As long as the mirror is a perfect reflector the image will be very faint, but when dew is deposited the mirror and its image become luminous. For observation purposes it is seen conveniently by a low-magnification eyepiece at *E*.

If it were assumed that the only difference in diffraction-effect between particles on a mirror and particles in suspension is that the former will produce twice as great an intensity as the latter, then it would be possible to calculate the distribution of

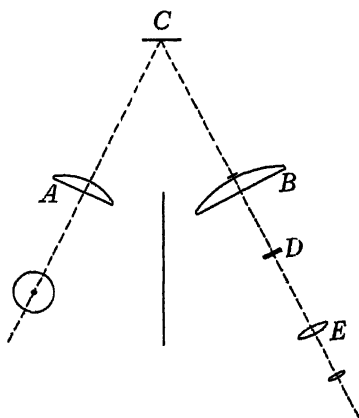


Figure 1. Diagram of optical system.

the diffracted light. This would require a knowledge of the particle-size, but since this can most easily be measured indirectly, by ascertaining the light-distribution, and since such an experiment will give the information required directly, there is little to be gained by a theoretical investigation.

The chief experimental difficulty is the instability of a dew film which precludes measurement of intensity at many points with one of the many instruments available. The difficulty was overcome by the following method which explored the whole field of 180° in front of the mirror in 2 seconds.

A mirror, fixed in the side of a glass tube so that it could be cooled with ether, was mounted vertically. Below it with its axis on the vertical diameter of the mirror was a spindle carrying an arm about 150 cm. long. A plane mirror, mounted at the outer end of this arm, reflected light falling on it from the fixed mirror on to a photocell. The latter mirror was illuminated by a beam having an aperture of 5° , and the moving mirror also subtended a similar angle at the fixed one. The shaft made a complete revolution in four seconds, and as it turned the scanning mirror

explored the field of light reflected and scattered by dew on the other mirror. The photocell was used with a single amplifying valve having the string of an Einthoven galvanometer so connected in the anode circuit that the deflections were proportional to light incident on the photocell. Therefore, at any instant the position of the string was a measure of the light leaving the fixed mirror in the direction of the scanning mirror at that moment. The movements were recorded photographically in the form of a (current, time) curve, which was readily converted into a polar-intensity curve from a knowledge of the angular velocity of the scanning mirror.

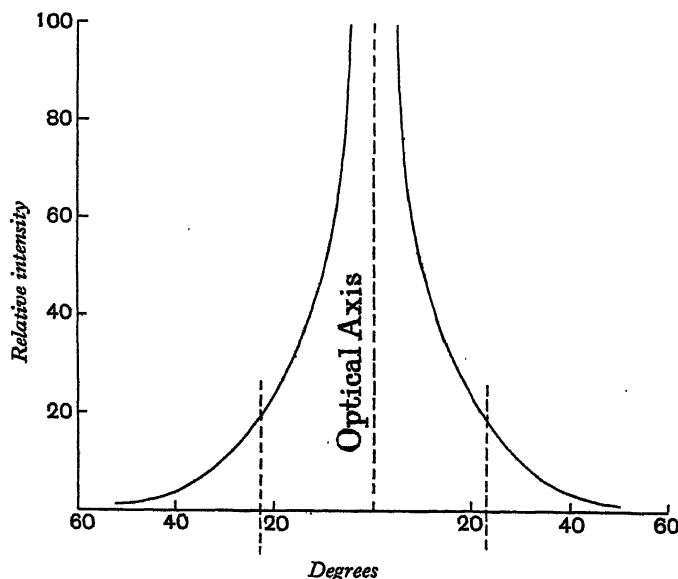


Figure 2. Intensity-distribution from dew-covered mirror.

The result for a wave-length range of 0.6 to 0.8μ , with the incident beam normal to the mirror is shown by the graph in figure 2. This shows that most of the diffracted light leaves the mirror within a total angle of 45° , and lens *B*, figure 1, in the optical system has been so arranged as to subtend approximately this angle at the mirror.

§ 3. THE AUTOMATIC DETERMINATION OF DEW POINT

The usual procedure for the estimation of the dew point is to permit air to bubble through ether, thereby cooling a surface on which the formation of dew is looked for. When it is observed the air flow is stopped, and the ether-temperature is noted when the last trace of dew disappears. This cycle is often repeated to confirm the first result. In the automatic determination the cycle is repeated continuously at intervals of from three to ten seconds depending on the dew point, air flow and other variable conditions of experiment. The temperature of the ether then oscillates only a fraction of a degree on either side of the true dew point, and the mean temperature, as will be shown later, is in very close approximation to it.

The eyepiece at *E* is now replaced by a photocell which is connected to a single-valve d.-c. amplifier. When the anode current exceeds a certain predetermined value it operates a relay which in turn closes a solenoid air valve, shutting off the air stream which produces a cooling effect by bubbling through ether or other suitable liquid. This is contained in a thin-walled brass tube, thoroughly lagged with asbestos except where the tube is cut away to receive the optically worked steel mirror. This is soldered on. The ether is thus in direct contact with the back of the mirror, which is less than 1 mm. thick. Stainless steel was chosen as the best material for the mirror on account of its thermal conductivity and its ability to take and retain a good optical polish.

It is essential that the supply of ether or other refrigerant be steady and the level constant, so a supply of about 150 cm.³ is contained in a small tank which feeds the apparatus through a float chamber, as in a carburettor. Under average conditions this quantity lasts for several hours.

The air valve is of simple construction, being an ironclad solenoid with a moving plunger of mild steel fitted with a stainless-steel needle which comes into contact with a gun-metal seating. A current of 0.15 A. at 2 V. will close it against a pressure of 10 lb./in.² As this valve is only an on-and-off control, a small tap is provided to adjust the flow.

In the apparatus which is shown, the gas-filled lamp has a rating of 24 watts at 12 volts. It has a screwed cap and the filament is vertical. Lenses *A* and *B* have focal lengths of 6.0 and 5.0 cm. with diameters of 2.2 and 5.0 cm. respectively. The distance from the mirror to both *A* and *B* is 9.0 cm. The lamp, lenses, valves, photocell and relay are enclosed in a metal box measuring 23 cm. × 14 cm. × 17 cm. which has an elongated aperture to pass the incident and reflected light. The tube with the mirror is carried at the end of a hollow arm, through which the ether is fed, by a ball joint permitting adjustment to the correct position. The ether-feed device and air valve also are secured to the base of the box.

The electrical circuit is shown in figure 3. It contains no novelties, and the only point worthy of note is the method of obtaining a current to oppose the steady anode current, so that it is possible to work on the steep part of the valve characteristic. It will be obvious that a current will flow through the relay coil unless the anode current flowing through *R* produces a p.d. equal to 2 volts. When the potential exceeds this value the relay is deflected in the direction which closes the circuit through the solenoid. To protect the somewhat delicate contacts of the relay from sparking an inductive surge-absorber consisting of a single-disc copper-oxide rectifier is used. The valve is of the 2-volt power type with a mutual conductance of 3.85 mA./V., and a standard photocell of talking-picture type is used with an applied potential of 80–90 V.

When the apparatus is working the air flow is intermittent, and to avoid excessive hunting the frequency of intermission must be as great as possible and this is secured by so adjusting the grid-bias that the relay trips with the minimum of dew. For example, if the relay will make contact when the anode current exceeds 5 mA. the grid-bias should be adjusted to make the anode current about 4.8 mA. with a

clear mirror. As the mutual conductance of the value is 3.85 mA./V. this means that the relay is being operated by a photoelectric current of $5 \times 10^{-9} \text{ A.}$, and the dew producing this will be barely visible to a human eye observing it directly, although it can easily be discerned by the optical arrangement described earlier.

For instantaneous temperature-readings a mercury thermometer is quite suitable, but a platinum resistance thermometer offers the possibility of remote reading and recording. A thermocouple may be used, but a single junction would not give quite the same accuracy as either of the other two alternatives.

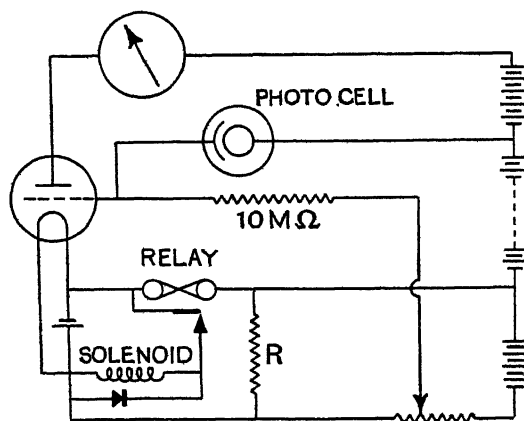


Figure 3. Electrical circuit.

§ 4. EXPERIMENTAL

The steel mirror is approximately 1 mm. thick, this being the minimum thickness with which optical perfection can be ensured, and it seemed that there must be a temperature-gradient in material of this thickness. To measure such a difference directly would involve the evaluation of small quantities, but an indirect measurement is feasible. With the correct manipulation or control, the outer surface is maintained at the dew point. If it is assumed that a difference of temperature exists between the inside and outside of the mirror, then it is logical to expect an increasing difference with rising air-temperature if the dew point is kept constant. Consequently, when the apparatus is working in an atmosphere having a constant water-content, a rise in the air-temperature will be accompanied by an apparent fall in dew point as shown by the ether-temperature. Experiments were made along these lines to determine the temperature-difference indirectly.

The tube with the mirror was placed behind a window in a miniature wind tunnel, so that air which was driven through the tunnel passed parallel to the plane of the mirror. At the inlet end the air was blown over wet- and dry-bulb mercury thermometers. These were shielded from radiation from a wire resistance mat, which farther up the tunnel provided the means for raising the air-temperature without affecting the water-content or its determination.

Early tests on the automatic apparatus showed that it did not work satisfactorily in a still atmosphere, and one purpose of the wind-tunnel tests was to find the effect

which air-velocity had on the readings. The same apparatus was employed, the velocity being measured with a Pitot tube in conjunction with a Threlfall gauge. It was convenient to make the two sets of experiments concurrently as the air-temperature and velocity could be changed very easily; thus for any particular dew point a number of readings were obtained for a range of temperatures and velocities. Some results are shown in figures 4*a* and 4*b*.

Figure 4*a* shows that considerable errors may be expected at low air-velocities, that is, at velocities of less than 200 cm./sec., and the points in figure 4*b* were all determined above this value. This latter diagram seems to deny the existence of

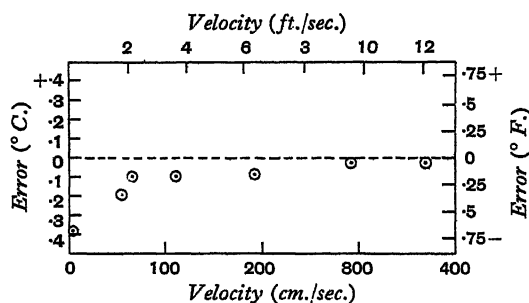


Figure 4*a*. Instrument error at different air velocities.

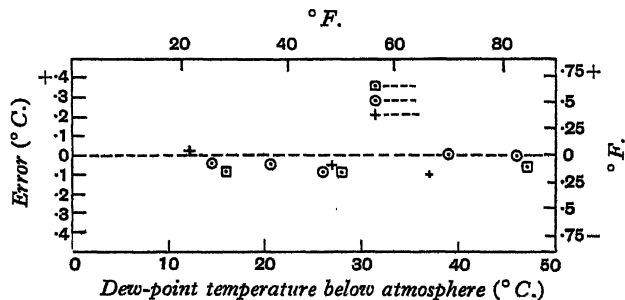


Figure 4*b*. Instrumental error at different dew-point depressions.

any temperature difference between the sides of the mirrors, since the error is not proportional to the difference between apparent dew point and air-temperature. In view of the constant discrepancy between the true and apparent dew points the thermometers used were rechecked carefully against fixed points and National Physical Laboratory standard without the disclosure of any explanation. Probably we must look for this to figure 4*a* which shows a decreasing error with rising velocity; it is probable that at still higher velocities the error would vanish. It may be due to a relatively stationary layer of air in contact with the mirror. Unfortunately apparatus was not available to test the validity of this inference.

That the error is due to absorbed radiation from the lamp is denied by the way in which the dew forms and evaporates. The centre of the mirror on which the light falls is the first part to be covered and the last from which the dew vanishes.

During these experiments the air flow through the ether with the solenoid valve open was the maximum that could be passed without liquid ether being bubbled out of the tube. This flow permits dew points 50° C. below air-temperature to be reached, but gives some hunting at low depressions. For the best results the air flow should be adjusted to the minimum which will give the necessary depression with certainty.

It may be concluded from the results that this apparatus permits the determination of the dew point with a possible error not greater than -0.1° C. provided that the air-velocity parallel to the mirror is greater than 200 cm./sec. and that the electrical controls are correctly adjusted.

§ 5. ACKNOWLEDGMENT

The instrument has been developed and used in the laboratory of the Cambridge Instrument Co. Ltd., and it is to the Directors of the Company that I am indebted for permission to publish this description.

DISCUSSION

Lord RAYLEIGH suggested that an optical system similar to that adopted by the author might be used for photographing finger-prints or for intensifying weak negatives. An image of the surface bearing the finger-prints or of the silver deposit in a negative could be formed by scattered light alone, the direct light being eliminated as in the author's apparatus.

Mr J. GUILD. It seems desirable, now that methods of ever increasing precision are being developed for measurements of this kind, to enquire to what accuracy the assumptions underlying the method are valid. In the original Regnault dew-point apparatus, of which these photo-electric devices are simply refinements, the fundamental assumption is that the temperature of the metal surface, when dew begins to form, is the temperature at which the air in its immediate neighbourhood is just saturated by its moisture content. No doubt this assumption was true enough to the kind of accuracy attained by the original dew-point apparatus, but it is by no means obvious that it is absolutely true. The formation of dew-drops on a highly polished surface is probably not a simple phenomenon, and it is quite possible that a certain degree of supersaturation is necessary before deposition begins. What is the existing evidence on this point? It is clearly necessary before we can usefully advance the precision of dew-point measurements to establish without doubt that the temperature at which dew condenses on a polished surface does not differ from the saturation temperature by an amount comparable with the precision of the instrument.

Dr L. SIMONS. Does the author find that the mirror retains its initial polish? Does not dust, having the same optical effect as dew, collect upon it in time?

Dr EZER GRIFFITHS. The method described for projecting the image of the surface on which dew is deposited is neat and should prove of practical value in

cases where the surface has to be situated at some distance from the point of observation. I used the photoelectric cell as a means for detecting dew some five years ago. The description of the arrangement will be found in a special report of the Food Investigation Board entitled "The measurement of humidity in closed spaces."

MR R. W. POWELL. I should like to know if the author has compared the value of the dew-point temperature as recorded by this automatic instrument with that obtained by the normal visual method. Such data would be of particular interest since it would appear that the automatic instrument tends to give somewhat low values.

With regard to the temperature-drop through the mirror itself the author states that "stainless steel was chosen as the best material for the mirror on account of its thermal conductivity." Just what is meant? The thermal conductivity of stainless steel is low compared with that of most metals. However, this is not actually of vital importance since the temperature-drop through the mirror in 'still' air conditions should not exceed 0.01°C . when the depression is 20°C . I assume that the experimental test was really made to determine if a temperature-discontinuity existed between the metallic surface and the cooling-liquid in which the thermometer was immersed. In view of the possibility of such a discontinuity I submit that it would be an improvement to measure the dew-point temperature by means of a thermocouple soldered to the metallic surface.

I should also like to ask how the true dew-point was determined, and to point out that if wet- and dry-bulb thermometers were suspended in the wind stream as described, the true maximum depression of the wet bulb would only be attained at the higher wind-speeds.

AUTHOR'S reply. In reply to Lord Rayleigh: A photometer based on the suggestion of measuring the light scattered by the silver particles has been constructed by Brentano, but he used a stop in a position equivalent to one immediately in front of lens *B*, figure 1. If the stop is used here it ignores the possibility of scattering from the surface of lens *A*. In practice, this cannot be ignored and the position of stop *D* shown in figure 1 is theoretically the most sound.

In reply to Mr Guild: There is no evidence in these experiments that the mirror surface is at the saturation temperature of the air when dew is formed. If it is not so then the resultant error is included in that shown in figures 4*a* and 4*b*.

It is found, as suggested by Dr Simons, that some dust does collect on the mirror, but the rate at which it is deposited seems to bear some relation to the density of the dew-deposit which is allowed to form. This apparatus works with a small density and although as a result it is sensitive to a minute dust-deposit, it is found that the effect of dust on the mirror is less serious with small dew-deposits. For the best working it is desirable to clean the mirror each day, and this necessity for frequent cleaning was one reason for the choice of stainless steel as the material for the mirror.

I am interested to note from Dr Griffiths's remarks that a photoelectric method has been in use for the detection of dew-deposit at the National Physical Laboratory. The vital difference between the two systems, however, is that this one utilizes the intense scattering which occurs at small angles to the truly reflected beam. More light is thus available for the operation of the photoelectric device from a given deposit of dew in this apparatus than in the one used at the National Physical Laboratory.

In reply to Mr Powell: The readings of this instrument were not compared directly with a normal manually operated visual instrument, but figures 4*a* and 4*b* show the difference between the readings given by the apparatus and the dew point as calculated from wet- and dry-bulb thermometer readings with the aid of the tables published by the United States Department of Agriculture Weather Bureau, and I have always found that the normal visual method gives results in agreement with these tables. A compromise had to be made in the choice of material for the mirror. It was necessary to choose a metal which would take and retain a good optical polish. In view of the need for high thermal conductivity, stainless steel was chosen. The results given in figure 4*b* show the magnitude of the instrumental error for various differences between dew point and atmospheric temperature. It is sufficiently small to be negligible for most humidity-measurements. If extreme accuracy is required then allowance can be made. The difficulties of fixing a thermocouple to the mirror surface so as to obtain the surface temperature would be great, and as its presence would hinder the cleaning of the mirror there seems to be no reason for thinking that it would give improved results. In checking the instrument, the effective air-velocity for the wet bulb was of course not overlooked, and correct conditions were maintained.

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HUE-DISCRIMINATION IN NORMAL COLOUR-VISION

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AND

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ABSTRACT. Hue-discrimination curves have been obtained for five normal observers; the apparatus and method of observation are described and the results discussed. Two minima in the discrimination curve are found at about 0.60μ . and 0.49μ . and a secondary minimum at 0.45μ . The curves are appreciably different from those normally reproduced in text-books, particularly at the red end of the spectrum where a secondary minimum has generally been shown. An analysis of the work of previous investigators, however, shows that the evidence for this secondary dip is very inconclusive.

§ 1. INTRODUCTION

ONE of the most significant characteristics of colour-vision is the power of distinguishing between the colour sensations evoked by different spectral radiations. The crude division of the spectrum into red, orange, yellow, green, blue and violet, is well known, but a more exact analysis of the colour-differences of neighbouring radiations is also possible. For instance, if we view two patches of light in a photometric field, one illuminated by a radiation of wave-length λ and the other by a slightly different radiation, of wave-length $(\lambda + \delta\lambda)$, then as $\delta\lambda$ is increased the two halves of the field become just noticeably different in colour. (It is important that the intensities of the two patches be kept equal, to ensure that only the hue-discrimination function is acting.) The value of $\delta\lambda$ will vary with λ and a curve can be obtained relating the two quantities. This curve is generally known as the hue-discrimination or hue-sensibility curve and most probably is closely related to the fundamental response or excitation curves. Its evaluation is therefore of considerable theoretical interest, as well as of practical importance in colorimetric work.

In the course of other investigations the authors had occasion to determine the hue-discrimination curves for their own eyes and were surprised to find that although the two curves obtained agreed quite well with each other, yet they were markedly different from the average curve usually reproduced in text-books or analysed in modern discussions of visual theory. The frequency with which the curve is referred to is a sufficient indication of its importance and the need for its reliable determination, and it was therefore decided to investigate the matter more fully.

The practical value of the data is that they enable us to know the significant accuracy of colour-measurements or colorimetric calculations and to measure the visual characteristics of an observer and to assess his value for work involving colour-discrimination, while their theoretical value lies in their forming a basis for the development of a satisfactory theory of colour-vision, for either the normal, the anomalous or the colour-blind observer. For these purposes there would not appear to be any call for the determination of a standard curve on the lines of the standard luminosity curve or the standard colour-mixture curves. It was therefore considered the better procedure to determine curves for a few observers only, under properly controlled conditions and with the necessary practice and adequate checking of the results, rather than to obtain a greater number of curves with the possible sacrifice of individual reliability.

§ 2. APPARATUS AND TECHNIQUE

The apparatus used was the Wright colorimeter, slightly modified to meet the special requirements of the experiment. A diagram of the optical system is shown in figure 1. Light from a pointolite lamp is focused on the slit S and made parallel by the collimating lens C . This parallel beam, after passing through a right-angled

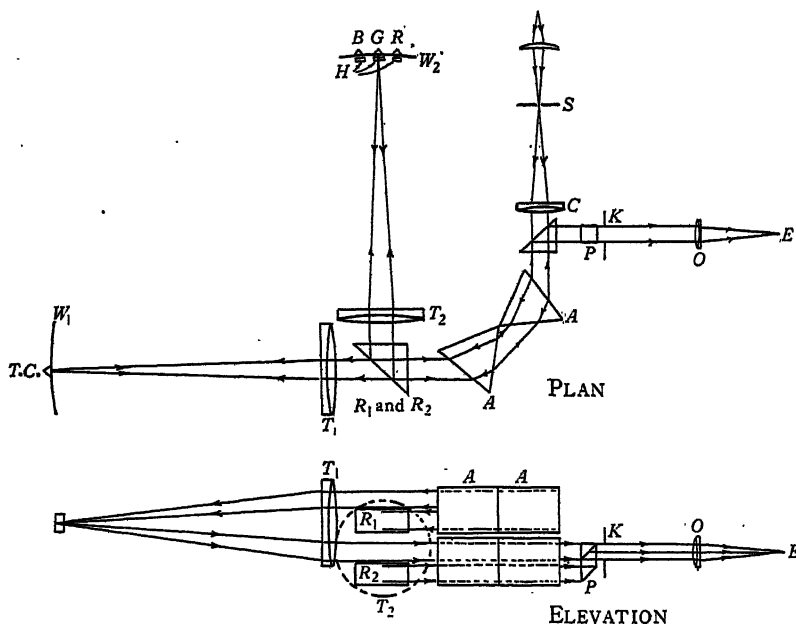


Figure 1. The Wright colorimeter.

prism, passes through the dispersing prisms A . The top half of the dispersed beam passes over the top of the right-angled prisms R_1 and R_2 , through the lens T_1 , and is brought to a focus in the form of a spectrum at W_1 . The lower half of the dispersed beam is reflected at 90° by the prism R_1 , passes through the lens T_2 , and

is brought to a focus in the form of a spectrum at W_2 . Three portions of the spectrum W_2 are reflected back by right-angled prisms R , G and B , and return through the optical system to the right-angled prism D where they are reflected on to the photometer prism P . When the instrument is being used as a colorimeter, these portions of the spectrum form the primaries, but in the present research they were used, singly, to form the comparison source. Any portion of the spectrum W_1 may be reflected back through the optical system on to the photometer prism P by another right-angled prism, TC . The photometer prism is so constructed that the two beams, from W_1 and W_2 respectively, are brought together into the neighbouring parts of a simple bipartite field, separated by a sharp dividing line. The aperture K limits the field of view and is of such a size that it subtends approximately 2° at the eye, which is placed at the focus E of the objective O . An exit pupil, of diameter = 0.040 in., is placed at E to limit the width of the spectrum entering the eye. To control the intensities of the primary beams, neutral wedges H , the positions of which are controlled by the observer, are mounted in front of the prisms R , G and B . It should be pointed out that neutralization of the dispersion of the beams is effected on their return through the system so that two parallel beams, one from W_1 and one from W_2 , fall on the prism D . The optical system also is so arranged that the returning light traverses a lower part of the system than that traversed by the incident light. This diminishes to a large extent troubles caused by back reflections from the various glass-air surfaces, and renders the apparatus effectively free from stray light. A fuller description will be found in a paper by W. D. Wright⁽¹⁾.

Owing to the existence of a small circular stop at E , instead of a slit, the light entering the eye is not strictly monochromatic. The integral effect of the light is to produce a colour sensation that can be matched with a monochromatic radiation, and when the apparatus is used as a colorimeter this arrangement is entirely satisfactory. But for a reliable determination of the hue-discrimination curve it is essential that the variable half of the field should be illuminated with a beam as nearly monochromatic as possible. This condition was obtained by placing a narrow slit in front of the prism TC in spectrum W_1 in such a position that a slit-image was formed in the centre of the exit pupil⁽¹⁾. During the experiment the width of the slit was adjusted so that at no part of the spectrum was the wavelength band greater than 0.0010μ , while at the blue end it was considerably smaller. The only disadvantage produced by this modification was the slightly streaky appearance of one half of the field. This effect, however, was very slight and insufficient to cause any discomfort or difficulty to the observer.

In the method adopted for measuring the steps, the other half of the field was illuminated with light from various fixed points in the spectrum W_2 and used merely as a comparison colour. There was therefore no need to take special precautions to ensure strict monochromatism in this beam.

The only other modifications in the apparatus that had to be made were the provision of a scale in W_2 in order to set R , G , or B at the required points in the spectrum, and the addition of a mechanism to enable the observer to control the position of the prism TC in the W_1 spectrum. A simple device consisting of a

drum, string, pulleys and counterbalancing weights provided a fine control, easy to operate and almost entirely free from backlash. The settings were, of course, read direct from the spectrum scale in W_1 and were quite independent of any backlash or variance in the mechanism.

Before any observations were made the observer was dark-adapted for about 15 minutes, and then the actual experiment was performed as follows. One half of the field was illuminated with light of a certain wave-length coming from spectrum W_2 , while the other half consisted of light of the same wave-length but coming from W_1 . The luminosities of the two colours were then adjusted to equality by means of the neutral wedge. When an accurate match had been obtained the observer very slowly moved the prism TC through the spectrum, at the same time keeping the luminosity equal for both halves of the field by means of the wedge control. A position for the prism was eventually found where the colours of the two halves of the field were just perceptibly different and the reading of the wave-length scale was recorded. The prism TC was then moved in the opposite direction until the colours of the two halves of the field were again just perceptibly different and the wave-length was again recorded. This process was repeated twice for each wave-length, and after a little practice it was found that readings could be repeated with a high degree of accuracy considering the nature of the observation being made.

If the repeat readings did not agree well, more were taken. The average for each reading was found and the difference between them represented two colour steps. Half this difference gave one colour step, but only approximately in view of the fact that the lengths of the steps vary continuously throughout the spectrum. The colour steps, or difference limina, were found at various wave-lengths, and curves showing this relationship were obtained. The curves were confirmed with a repeat series of observations, and in the case of the authors the observations were repeated three or four times.

§ 3. RESULTS

It has been suggested in some quarters that for the results to be of full significance the determinations should be made at a uniform intensity-level throughout the spectrum. Laurens and Hamilton⁽²⁾, however, have shown that the size of step is practically independent of intensity over quite a wide range, and this point was investigated and confirmed by the authors, although it was found that when the intensity was greatly diminished, say to about 0.01 of its original value, the colour limen did increase appreciably. As a uniform intensity-level would have involved a very low intensity throughout the experiment, it was considered better to allow some variation, but between wave-lengths 0.65μ . and 0.48μ ., the range was only 4 to 1, with an average retinal illumination of the order of 70 photons, while the total range to the blue end of the spectrum was about 20 to 1.

Considerable scattering of the points was obtained in the initial observations, in consequence of lack of familiarity with the apparatus and the type of observation, but reasonably consistent and reproducible results were obtained after practice.

A smooth curve had, of course, to be drawn through the points, but with rare exceptions no point lay off the smooth curve by more than 10 per cent of the value of $\delta\lambda$ at that point.

In figure 2 the smooth curves for five observers are given, and a mean of their results is shown in figure 3. The similarity in general characteristics of all five curves is very striking. The magnitude of the steps naturally varies from observer to observer, but each curve shows a broad minimum at about 0.60μ . and a somewhat sharper minimum at about 0.49μ . With one exception each curve has a secondary dip at the violet end of the spectrum between 0.45μ . and 0.46μ ., but what is more

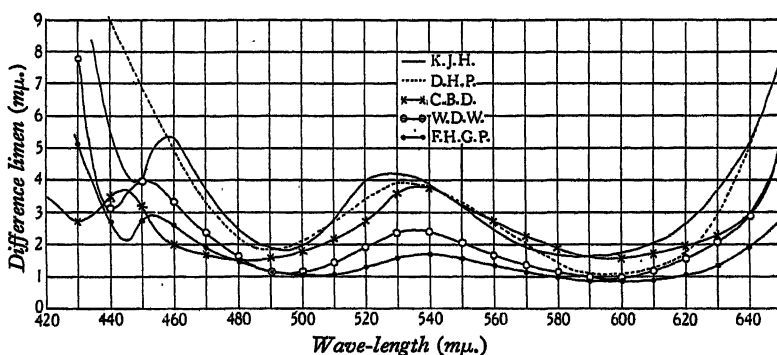


Figure 2. Hue-discrimination curves for five normal observers.

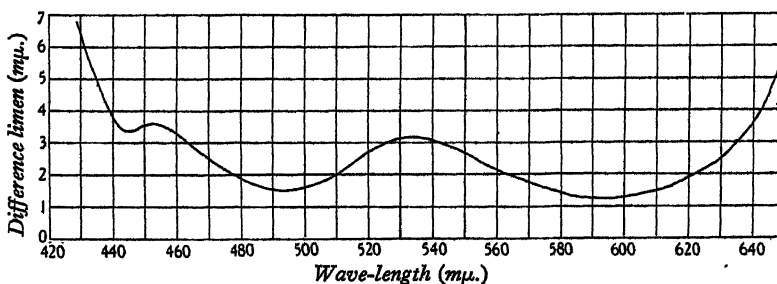


Figure 3. Mean hue-discrimination curve for five normal observers.

important, in relation to previous investigations, is that there is no secondary dip whatever in the red. In the next section it will be shown that a dip of this sort at about 0.63μ . has been found in a number of previous investigations, and its absence is the most striking difference between these results and those of earlier investigators. As it was important to ensure that observational errors were not masking the dip, that region of the spectrum was checked with particular care. The scattering of the points was probably greater here than at any other point in the spectrum, possibly on account of the greater effect of colour-adaptation in the red, but no indication of a dip was obtained.

Some doubt has also been raised as to the existence of the dip in the violet, and it has been mentioned above that for one observer no dip was found. This result

may arise from the decreased sensitivity, due to the lower intensity of the field, as a result of which the steps may have been large enough to mask any dip that might exist. On the other hand, luminosity-measurements made on this observer showed that his blue luminosity was not appreciably lower than for the normal observer.

The curves as a whole have the characteristics that might be anticipated from a cursory glance at the spectrum. The part of the spectrum where a minimum step exists must obviously occur where there is a rapid change in colour; thus in the yellow where the colour turns redder on one side and greener on the other, in the blue-green where it turns bluer on one side and greener on the other, and in the violet where it becomes redder or bluer, minimum steps would be expected. But between $0.61\ \mu$. and $0.65\ \mu$. the colour changes steadily to a deeper and deeper red, and the existence of even a secondary minimum would be most unexpected. A rough analysis of this sort could not be used to discredit direct observations if they indicated a minimum, but it can be used to show that the curves now obtained have a good deal of logic to support them.

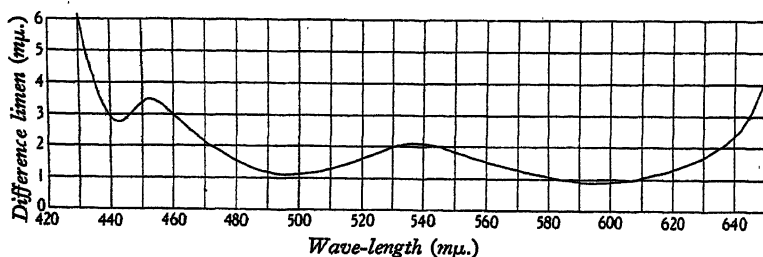


Figure 4. Mean of authors' hue-discrimination curves.

The process of averaging the curves inevitably tends to flatten out the dip in the violet region, and for this reason an average of the authors' curves alone has been made and is given in figure 4. This curve is perhaps more representative of the normal eye than figure 3, for if we imagined a very large number of curves to be available the dip in the violet would probably be averaged out altogether. Hence an average curve may not necessarily represent the visual characteristics of a normal eye. The data for the authors' eyes were obtained after more practice and were repeated more often than in the other cases, and as the two curves were remarkably similar, the mean curve of figure 4 is perhaps more valuable than figure 3. Although the point is of no special theoretical significance, it is of interest to note that the data in figure 4 imply that the authors can distinguish 150 different hues in the spectrum.

It should be mentioned that a preliminary test on the colour-mixing characteristics of the observers was made and none of those for whom curves are given were abnormal. A sixth observer was found to be anomalous, but although his discrimination curve was taken publication will be deferred until a more comprehensive study of anomalous vision has been made.

§ 4. PREVIOUS INVESTIGATIONS

The chief experimental investigations during the past 50 years have been those carried out by König and Dieterici⁽³⁾, Steindler⁽⁴⁾, Jones⁽⁵⁾, and Laurens and Hamilton⁽²⁾. Valuable theoretical discussions have been made by Helmholtz⁽⁷⁾ and Judd⁽⁹⁾.

König and Dieterici⁽³⁾ tested their own eyes by making the two halves of the field similar instead of just noticeably different. By repeating the setting 50 times the mean error of adjustment gave a measure of the sensitivity for the particular wave-length tested, and similar experiments repeated throughout the spectrum enabled the complete hue-discrimination curve to be drawn. The apparatus and conditions of observation appear to have been satisfactory. The two curves thus obtained are shown in figure 5. It should be noted that this method of measuring the sensitivity must give appreciably smaller values for $\delta\lambda$ than those obtained by the just-noticeable-difference method. It will be seen that no dip in the red was found.

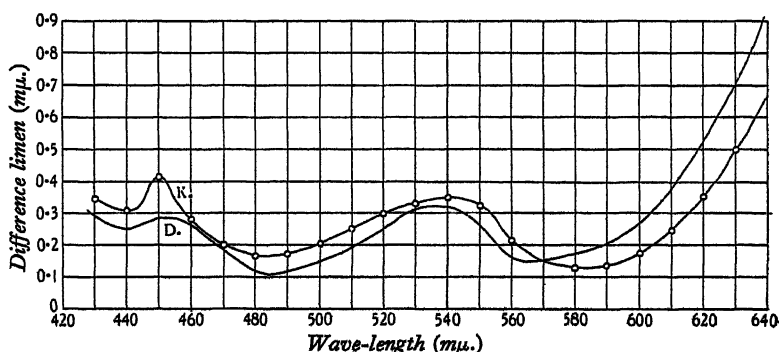


Figure 5. Hue-discrimination curves of König and Dieterici⁽³⁾.

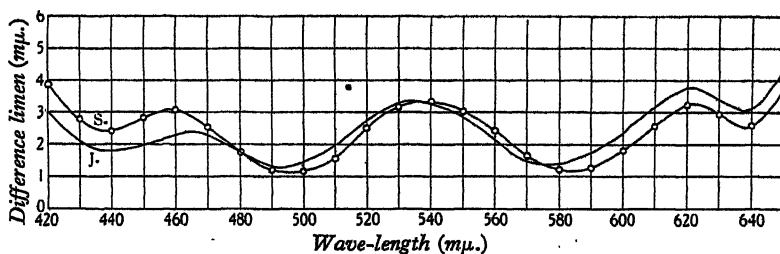


Figure 6. Hue-discrimination curves of Steindler⁽⁴⁾ and Jones⁽⁵⁾.

Steindler⁽⁴⁾, using a concave grating, obtained a first-order spectrum 85 cm. long. She made, on 12 normal observers, measurements of the minimum change of wave-length perceptible as a difference of hue between two juxtaposed fields. The precaution of equating the luminosity of both halves of the field was not generally adopted, and the field of view was apparently of a rather low intensity. The value of her results seems rather doubtful, especially as she obtained a very extraordinary curve for the hue-discrimination of colour-blind (protanopic) observers. Her mean curve for the normal observers is given in figure 6, curve *S*.

Jones⁽⁵⁾ investigated the hue-discrimination of only one eye, his own, but the observations appear to have been made under proper observational conditions. Some instrumental difficulties are recorded and although these are reported to have been overcome, the work was not extended to other observers as originally intended. The curve he obtained is also shown in figure 6, curve *J*; the close agreement with Steindler's curve is somewhat unexpected, especially as the secondary dip in the red occurs at a longer wave-length than in any of Laurens and Hamilton's results. Both Steindler and Jones give secondary minima in the violet.

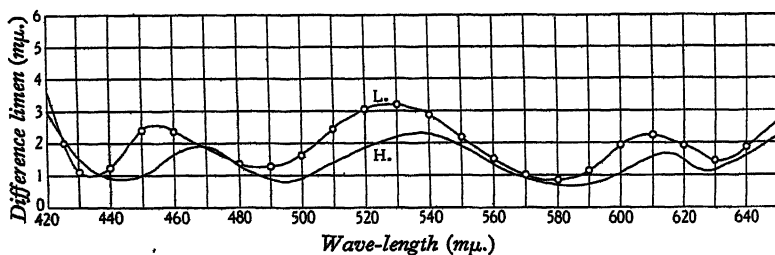


Figure 7. Hue-discrimination curves, each of which is the average of 16 complete series: Laurens and Hamilton.

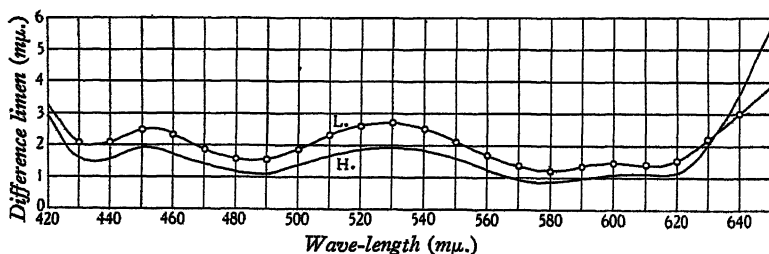


Figure 8. Hue-discrimination curves based on the simple averages of the values of the difference threshold at every 10 mμ. 16 tests on both Laurens and Hamilton.

Laurens and Hamilton⁽²⁾ obtained results for 10 normal observers. Their first apparatus, which was used to obtain data for 7 subjects, was subsequently discarded in view of certain disadvantages. Four subjects, two of whom were Laurens and Hamilton, were tested with an improved apparatus, but the experiments cannot be regarded as very satisfactory since it was necessary for an assistant to make the changes in wave-length. The observer was required to state whether he observed a colour-difference or not as the sizes of the steps were increased. The point at which a colour-difference was noticed was recorded and the sizes of the steps were deduced from these readings. Anyone familiar with limen-measurements will realize the unreliability of the results made on this basis, unless a large number of answers are obtained and the results subjected to the proper analysis of observations. Moreover, only a very low intensity-level (4 photons) was used. These conclusions are confirmed by the considerable variations shown even among the curves for the same observers. Thus in figures 7 and 8 two sets of data for the

same observers, Laurens and Hamilton, both taken on the improved apparatus, are reproduced. In the region that is most in doubt, the red, a marked difference between the two diagrams is seen. Evidently no evidence for or against the existence of a secondary dip can be deduced from these results.

Tyndall⁽⁶⁾ has recently published a hue-discrimination curve for his own eye that shows a very small dip in the red. The dip, however, is so small that the observations hardly justify its existence.

Helmholtz⁽⁷⁾ carried out a theoretical investigation of the relation between König's fundamental sensation curves and the hue-discrimination curve, and deduced a result in remarkably good agreement with König's discrimination curve given above, which shows no dip in the red. The basis of Helmholtz's calculations was criticized by Schrödinger⁽⁸⁾, but the curve obtained by the latter was substantially the same.

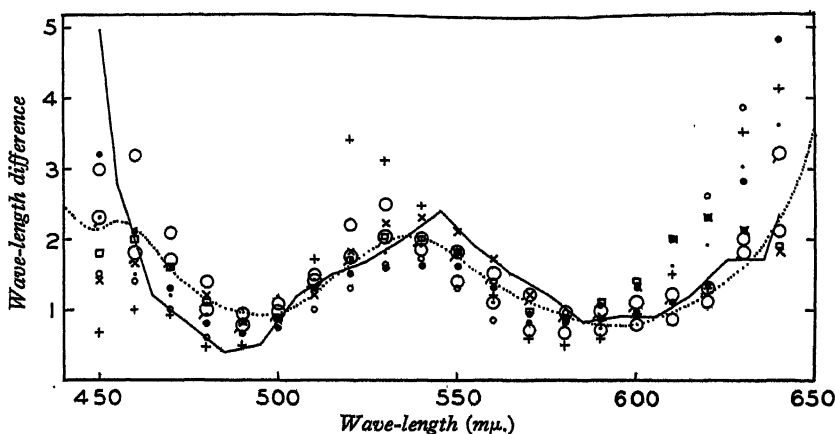


Figure 9. Experimental results from various observers as given by Judd. Continuous line represents Judd's theoretical curve; dotted line represents curve shown in figure 3. • König¹; ○ Dieterici; ● König²; + Exner; □ Steindler; ○ Tyndall; ○ Uhthoff; × Jones; — from empirical law.

Judd⁽⁹⁾ has analysed some of the experimental data on hue-discrimination and reproduced them in one diagram, which is also shown here in figure 9. He has developed a theoretical curve to fit the points approximately; this is shown by the continuous line in figure 9. The dotted curve is the mean curve of figure 3 of the present paper, superposed by the authors to show the extent of the agreement. This is very satisfactory, although it must be admitted that averaging a number of different investigations will always tend to smooth out any secondary minima that may exist.

Houstoun⁽¹⁰⁾ discussed the need for a change in colour-quality in the red if a secondary minimum really existed. It has been suggested that the red might become slightly blue, but modern colorimetric measurements have shown conclusively that this does not occur.

§ 5. CONCLUSIONS

How much weight to attach to various investigations is difficult to decide, but in this case the difficulty could be avoided by ascribing the disagreement of the results to the variation in colour-vision of the observers. Yet the authors feel that this is not the correct answer to the question. They believe that, while variations in detail must be expected from observer to observer, the general characteristics of hue-discrimination do not vary in the manner required to include, under this head, all the variations that have been reported.

The review of previous work has shown that there are at least as many data in agreement with the curves given in this paper as in disagreement. Yet for some reason the curves usually quoted in text-books and elsewhere have almost invariably been those having the secondary dip in the red.

At present little can be said beyond an expression of hope that it will be possible in the near future for some other investigator, with different apparatus but using the proper conditions and precautions, to repeat the experiment with a number of normal observers. It is anticipated with confidence that the results obtained here will be generally confirmed.

§ 6. ACKNOWLEDGMENTS

In conclusion the authors desire to express their very sincere thanks to those who spent considerable time and trouble in making observations, to Prof. L. C. Martin, and to the Medical Research Council for their financial assistance and for permission to publish these results.

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DISCUSSION

Mr C. R. DARLING. The late J. W. Lovibond informed me many years ago that in using his tintometer to match different parts of the red end of the spectrum, he found one part which presented more difficulty than the portions on either side. He was of opinion that this was due to the human eye being less sensitive to this particular band than to the remainder. The conclusions reached in the present paper do not confirm this view, but as the question is of practical importance it would seem desirable to make a special investigation from the standpoint of colour-matching.

Prof. L. C. MARTIN. I think the authors' results deserve careful attention, as experiments of this kind make very stringent demands on the perfection of the apparatus. In this case the freedom from stray light, and the good observing conditions generally, lend considerable weight to the conclusions reached. It might perhaps be suggested that some attention should be directed in the paper to the influence of the intensity-drop at each end of the spectrum, which may, I suppose, be taken to explain the rapid increase in the limen at the ends of the curve. How far would a red maximum and minimum have to be displaced towards the end of the spectrum before being masked completely by the intensity effect? I quite agree with the idea that individual differences in the curve may be of very considerable interest in the discussion of theories of colour-vision and its variations.

Dr W. S. STILES. The authors mention that their own hue-discrimination curves were determined on several occasions. It would be interesting to know the order of magnitude of the variations exhibited in these repeat observations, and whether any general change throughout the spectrum occurred which could be interpreted as a distortion of the curve or a bodily shift up or down. Marked day-to-day variations are frequently observed in brightness-difference threshold measurements and must be attributed to changes in the visual mechanism. If the three mechanisms postulated by the trichromatic theory are subject to such changes and are so in different degrees, distortion of the hue-discrimination curve may result. The authors are, I think, a little hard on the method of determining thresholds by answers given by the subject. Admittedly laborious, the method is fundamentally sound and can be employed under conditions where setting by the subject is out of the question. No criticism of the use of setting by the subject in the present investigation is intended.

Mr J. GUILD. In this paper the authors present us not only with new observations on wave-length discrimination by the eye in virtue of the accompanying change of hue, but also with a very useful digest of previous results. The importance of fresh observations in these discrimination problems cannot be over-emphasized. The determinations are of a very difficult kind and peculiarly liable to systematic

errors, and the more independent determinations we have the less likely it is that the same systematic errors will pervade them all.

The authors quite correctly perceive that in matters of this kind it is much more important to obtain thoroughly reliable results for one reasonably normal observer than to devote the same time to obtaining the average results of a cursory examination of a large number of observers. The statistical boggy plays too large a part in the general attitude to problems of this kind. Where the object of an investigation is to set up some convenient social standard, as, for instance, a "standard observer" for the purpose of giving definiteness to technically important photometric and colorimetric quantities, statistical data representing a hypothetical "average" or "normal" individual are of importance; but where the object of an investigation is to establish certain characteristics which are inherent in the nature of the human machine, it is much better to devote the available time to the careful examination of one individual, or at most two or three, than to spend the same time rushing a large number of unskilled subjects through tests of a necessarily hurried character.

The authors also point out, what is generally overlooked, that average results may in fact minimize or conceal characteristics which are found in every individual.

In liminal experiments the question of tolerances is of the utmost importance. In fact the experiments are *prima facie* determinations of tolerances in some specified variable. If this were the only experimental variable entering into the experiments everything would be straightforward, but it is not; the brightness varies continuously along the spectrum provided by the instrument, and has to be adjusted to equality at each observation. In theory the observer, having made this adjustment, has nothing to detect except difference in hue. In practice the equalization of brightness is only approximate: there is a practical tolerance in the intensity-adjustment as well as in the hue-adjustment. When dealing with liminal differences it is impossible to distinguish completely between differences in hue and differences in brightness. The observer, having done the best he can to equalize the brightness, assumes that any difference he sees is difference in hue, but if the brightnesses are not in fact equal, the difference he sees may be compounded of a difference in brightness and a difference in hue, each of which by itself may be subliminal, though together they produce an appreciable change in sensation.

We cannot assume on *a priori* grounds that the effects of the brightness-tolerance, even if non-systematic, will be eliminated in the mean of a large series of observations, but we can be sure that they will not be eliminated if there is any predisposing cause of systematic error in the brightness-adjustments, and it is beyond question that in all colour-matching apparatus there are factors which predispose the various tolerances to be more on one side of the "true" adjustment than the other. To discuss these factors would occupy too much space, but they may easily be responsible for the fact that some investigators obtain results exhibiting features which are absent from those obtained by others, and we are faced also with the more disquieting possibility that since all investigations of this kind have had much

in common as regards general experimental method they may be affected in common by certain systematic errors.

With regard to the most important difference between the present results and those hitherto regarded as most reliable, namely the absence of a minimum in the red, this is certainly more in accordance with my own experience obtained in other ways.

I also agree with the authors that there is no theoretical reason so far known for expecting any such minimum; though too much stress must not be laid on this, as the theory of the relation of the wave-length limen to the other quantitative facts of vision is still, in my opinion, on a very tentative and insecure basis. However, such theoretical guidance as we yet have indicates that there should be no secondary minimum in the red. Thus in so far as the present results differ from others I think they are better, but I cannot feel quite so certain that in every respect in which they all agree they truly represent exactly what they profess to represent.

I think that on several grounds the best way to make liminal determinations is not to determine the limen directly but to deduce it from the spread of a large series of attempts at exact matching. This eliminates a number of psychological elements which enter into the direct method, though it is still subject to possible systematic errors arising from instrumental factors.

As far as I can see the only way to eliminate these, by either the direct or indirect method, is to accumulate results obtained with apparatus differing as much as possible in its mode of operation. In particular, I think it might make an appreciable difference if matters were so arranged that the range of the spectrum involved in a set of observations were of constant brightness throughout, so that the operation of the wave-length drum produces change of hue only and no accompanying change of brightness to be remedied by the auxiliary brightness-control. This would be difficult but should not be impracticable.

I hope that Dr Wright and his colleagues will continue to bring their experimental skill to bear on these visual problems, for the work is very much needed.

MR T. SMITH. The authors have referred to the dangers of combining results reached with different eyes, but this only increases the importance of making the fullest use of information obtained for the same eyes. I do not know whether Dr Wright has determined the visibility function for his own eyes, but he has certainly carried out much work on colour-matching. I should like therefore to ask him whether he has been able to infer from his own results in this and previous work any conclusions bearing on hitherto doubtful points in the theory of vision other than those mentioned in this paper, which relate to his last investigation alone.

AUTHORS' reply. In reply to Mr Darling: We should suspect that the difficulty experienced by Mr Lovibond in matching a certain part of the red end of the spectrum with his tintometer was due to the nature of the colour-filters used rather than to any reduced sensitivity of the eye in that part of the spectrum. The problem really concerns the colour-mixing characteristics of the eye, and no results

on colour-mixture obtained in recent years have suggested that a band in the red end of the spectrum is harder to match than the radiations on either side. The only bearing that hue-discrimination data have is as an indication of the limits within which two colours will still appear to be matched. If Mr Lovibond's idea that the eye is less sensitive to the particular band were correct, then actually that colour would be easier rather than more difficult to match, because the range over which a match would appear to hold would be greater.

Prof. Martin draws attention to the effect that the low intensity at each end of the spectrum might have in producing large hue-discrimination steps. It is improbable that any action of this sort is at work at the red end, since, at a wave-length of 0.65μ , the steps have already become large although the intensity is still high. A red maximum and minimum could hardly be masked by an intensity effect, since the steps would become large as a result of the small hue-discrimination before they became large as a result of low intensity. At the blue end of the curve there is little doubt that some of the increase in the size of step is due to the low intensity.

The query raised by Dr Stiles regarding the manner in which our hue-discrimination curves varied on different occasions cannot be answered very conclusively. One of us (F. H. G. P.) found little difficulty in repeating his curve to a surprisingly close degree on different occasions, but the other found that his sensitivity as a whole was liable to vary, producing a general increase or decrease in the size of his steps right through the spectrum. No distortion of the curve was found other than that due to accidental variations, although the possibility that changes in the visual mechanism may produce changes in the discrimination curve cannot be ignored. No evidence of such an effect was obtained.

We did not intend to convey an impression of distrust towards the method of determining thresholds by answers; our criticism was directed towards the manner in which the test appears to have been carried out by Laurens and Hamilton and not to the test in itself. The method is, we believe, perfectly sound for the usual type of threshold observation if correctly conducted. Nevertheless, in this case, in view of the simultaneous action of intensity and colour limina, the method of answers calls for very careful application and analysis if the results are to mean anything. The discussion below is particularly relevant to this point.

It is very gratifying to find that Mr Guild is in agreement with so many of the points we have made and to note that from his own experience he would not anticipate any dip in the red. We do not, however, share Mr Guild's doubt as to the quantities really represented by the hue-discrimination curve. His analysis of a colour limen into a subliminal intensity-difference and a subliminal hue-difference is correct for what we may call a static observation, that is an observation in which we merely view two fields and decide whether a difference exists or not, without having the power to control either the intensity or the wave-length of the two patches. But in the method of observation we adopted, the wave-length of one half of the field was altered and then the intensity of the other half was adjusted to see whether any difference that initially existed disappeared. The observer was only satisfied in his setting when he arrived at a wave-length step that produced a just-noticeable difference when the intensities of the two halves were exactly the same.

Although it might be impossible to say when this equality held, yet since the intensity of one half could be made greater or less than that of the other, then at some intermediate position they must be equal. This state was observed with all the other states, and if the colour-difference had been subliminal, no difference would have been seen at this point and the observer would have increased his step until a just-noticeable difference was perceived. The value finally recorded is therefore a colour limen alone and not a combination of intensity and colour limina.

On the other hand, this would not apply in the method of matching preferred by Mr Guild. In this method the observer would have to alter the intensity and wave-length until the two halves appeared alike, which would imply that a subliminal intensity-difference plus a subliminal colour-difference were together still below the threshold. It would be impossible to separate one from the other, and the final distribution of the points would be a complex function of the two limina. Thus this method is actually more and not less uncertain than the one we have used. An instrument in which the intensity was automatically adjusted to a constant level would no doubt be of value, but even there the two halves of the field would have, initially, to be brought to the same intensity by eye, and a subliminal error in this setting would produce a systematic error of the very type that we wish to avoid.

We conclude from this that the direct determination of the colour-step is, after all, the best method to adopt and the results so obtained do in fact represent the quantities that they purport to represent. This does not mean that we can immediately relate the discrimination curve to the visual mechanism; that will undoubtedly be a difficult process, and to illustrate the difficulty we need cite only one factor, namely adaptation, that must play an important part in determining the shape of the hue-discrimination curve.

In reply to Mr Smith's query regarding doubtful points in the theory of vision, both of us have determined our luminosity curves, trichromatic coefficients of the spectral colours and, of course, our hue-discrimination curves. These results do not differ seriously from previous determinations of the same functions except at the points mentioned in this paper. Any theory of colour-vision must account for these fundamental experimental results, but they do not provide new information of the type that assists in the evolution of a more satisfactory theory. Work on adaptation recently published* has, however, led to some significant conclusions and it would seem that more complete information on the various characteristics of colour-blindness provide the other most hopeful avenue of attack. Work on these lines is in hand, but until the results are completed we should prefer not to discuss theories of vision in detail.

As a complete set of curves may be of interest to others working in this field, we hope to publish our luminosity, colour-mixture and hue-discrimination curves shortly with, if possible, the addition of some measurements on saturation-discrimination.

* *Proc. R. S. A.* April. 1924.

A HIGH-SPEED MOTION-PICTURE TIMING-SYSTEM

by E. A. SABINE, Technical Consulting Department,
Western Electric Company Ltd

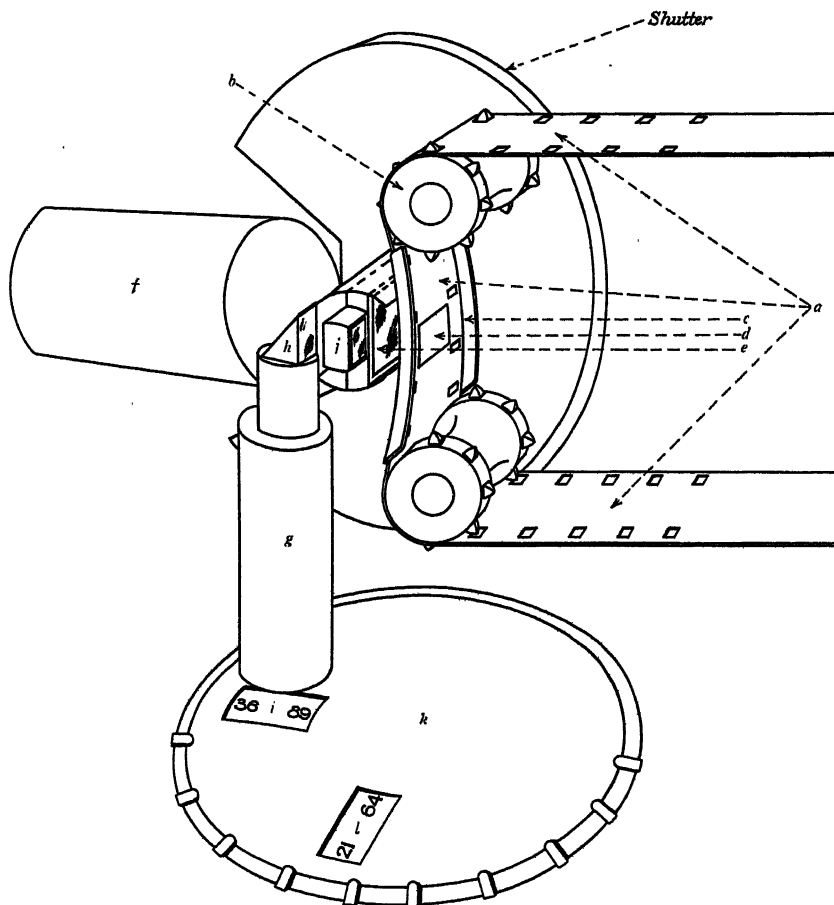
Demonstration given on March 2, 1934

§ 1. GENERAL DESCRIPTION

THE high-speed timing-system to be described was developed by the Bell Telephone Laboratories in conjunction with the Eastman Kodak Company and consists fundamentally of three main elements: a high-speed motion-picture camera, a high-precision electric clock, and a frequency-generator employing a tuning-fork to control the alternating current actuating the clock mechanism. The camera, which uses standard 16-mm. reversal safety film, has two lens systems so arranged that, when the camera is used to photograph any occurrence, the moving dials of the electric clock are also simultaneously photographed upon each frame of film beside the picture. Upon viewing or projecting the image so made, the time at which any event occurred can thus be read immediately from the direct time-record given with the picture of the occurrence.

The camera is available in two models, fundamentally similar but differing as regards the driving-motor and various secondary features, one being a high-speed model taking up to 250 frames per second and the other an ultra-high-speed model taking from 300 to 2000 frames per second. Owing to the excessive noise, vibration and wear, and the expensive construction and upkeep which would be inherent in a camera of conventional intermittent design if run at high speeds, such mechanism would be highly undesirable for this purpose, and the cameras are, therefore, of the continuous-movement type wherein all moving parts operate at constant speed. The film *a* tensioned by means of a spring-mounted top sprocket *b* is pulled continuously across a gate *c* having an aperture *d* slightly larger than the film-frame size in the vertical dimension. The projection of the image on to the moving film is accomplished by means of a uniformly-rotating plane-parallel plate of glass *e* which is interposed between the lens *f* and the film and acts as a plane prism. As the prism revolves the effect is to move the image in the film-plane downwards at the same speed as the film during the instant for which the shutter is open, thereby enabling a sharp picture to be obtained. Two pictures are thus made at each revolution of the plane prism, and every frame on the film is exposed. Framing is accomplished either by using an external mask or by means of small uniformly-rotating blades located respectively at the top and bottom of the picture aperture. The edges of the blades follow the frame lines of the picture down as the film moves. An auxiliary lens *g* and prism system *h* projects an image of the timing dials *i*,

suitably illuminated, through the rotating prism *j* so that this image is registered on the side of the film beside the picture in a manner similar to that in which the sound track is registered on sound films, except that in the present case the image of the timing dial is complete and appertains to the action photographed upon the frame beside which it appears, whereas sound track is of a continuous nature and the registration of sound applying to any particular frame is displaced approximately $14\frac{1}{2}$ inches in advance of the frame.



The high-speed or type-I camera is equipped with a lens-turret mounting, a $1\frac{1}{2}$ -in. F 2 Kodak anastigmat lens and a 4-in. F 4.5 Kodak telephoto lens and the ultra-high-speed, or type-II, camera is fitted with a single $1\frac{1}{2}$ -in. F 2 Kodak anastigmat lens; other lenses can readily be fitted if desired.

Speed-control of the type-I camera is effected by an electric governor, the setting of which can be varied by means of a speed-control knob at the rear of the motor. In the case of the type-II camera the speed is controlled by means of a rheostat in association with a series motor which for short periods can be considerably overvolted. Under such conditions the motor can be made to drive the camera

at such a speed that the motor itself runs at about 20,000 r.p.m. Internal gearing of the camera increases this speed up to 80,000 r.p.m. of the shaft which rotates the plane parallel prism. Since two images are registered on the film at each revolution of the plane prism, it follows that the linear speed of the film can be about 160,000 pictures per minute or approximately 2600 pictures per second.

In practice, excellent photographs have been secured at 2000 frames per second, and these when projected at normal speed give slow-motion pictures about a hundred times slower than the original action. This is thirty times slower than ordinary slow motion or fifteen times slower than the ultra-slow motion of the cinema.

§ 2. ELECTRIC-MOTOR CLOCK UNIT

The high-precision timing system which is an important feature of this apparatus consists of an electric clock which also is available in two types. The type-I clock unit, used in conjunction with the type-I camera, consists of an electric clock having three concentric dials reading minutes, seconds and hundredths of a second respectively to a total of 59 minutes, 59.99 seconds without repetition.

The type-II clock unit, used in conjunction with the type-II camera, consists of an electric clock having two concentric dials, one rotating once a minute and divided into 60 divisions for seconds and the other rotating once a second and graduated into 500 divisions each corresponding to 0.002 sec. Each division is further subdivided by a diagonal line which when read with reference to a stationary central vertical line permits time to be read down to 0.001 sec.

The dials are actuated by a specially developed salient-pole electric motor driven by alternating current, the frequency of which is regulated by a thermostatically controlled tuning fork calibrated to 200 c./sec. For short periods not exceeding 2 minutes the accuracy of the timing system with reference to the total time elapsed is within 0.05 sec. For longer intervals the precision is within 1 part in 25,000. In comparing closely adjoining pictures these limits do not, of course, apply, and it therefore becomes feasible to read to 0.001 sec. in such cases.

Two windows are provided for observing the position of the clock dials; they are cut in the resetting-plate *k* which is turned in a clockwise direction to reset the dials after each occurrence has been timed. One of the windows *l*, illuminated by two automobile head-lamp bulbs and small condensing-lenses, is located directly under the auxiliary lens-and-prism system, and reveals the dials that record absolute time. It is the image of this window which is photographed upon the film. Since, however, this window is not visible to the operator when the camera is operating, a further window *l'* is provided at an angle of 90° to the left of the objective window. The reading as observed in this window will, of course, be 15 minutes, 15 seconds and 25 hundredths in advance of the absolute time, except when the dials are in the reset position prior to starting. In this position the hundredth second dial is advanced 0.007 sec. in order to compensate for the time required for the operation of the magnetic starting clutch, and the time which is then indicated by the dials in the observation window is 15 minutes, 15 seconds and 25.7 hundredths.

The clock may be started or stopped at the camera location by means of two momentary-control keys located on the clock base, so arranged as to discharge polarized condensers in opposite directions and thus actuate relays which engage pawl-and-ratchet clutch mechanisms which, in turn, positively start or stop the clock dials. Alternatively the timing system may be started by means of a switch from some location remote from the camera.

§ 3. THE FREQUENCY-GENERATOR

The frequency-generator unit is a portable unit containing an automatically temperature-controlled tuning-fork and an amplifier to increase the output-level to a suitable value for the operation of at least two motor clock units. The primary purpose of this unit is to provide a sufficiently precise basic time rate for the system, and a secondary service is to provide operating current for the circuit.

The tuning fork vibrates at 200 c./sec., the vibration being started and sustained by the interaction of magnetic coils. Its temperature is controlled by electric heater elements which are in turn controlled by a mercury column thermostat embedded in the metal of the fork. The fork assembly is sealed in a heavily heat-insulated metal enclosure. This heat-regulation is such as to permit the fork to maintain the required precision over a temperature-range of -20° to $+120^{\circ}$ F. The primary requirement of the fork is temperature stability and it is, therefore, essential that the fork be connected and allowed to reach the stable temperature for at least one hour before time observations are made. The fork will maintain a precision of 1 in 25,000 over the previously mentioned temperature-range, with the commercial variations in the gain and characteristic of the amplifier, if the specified requirements as to operating-voltage adjustment and circuit-operation checking are correctly observed.

§ 4. CONCLUSION

In conclusion, it will be evident that the performance of this timing-system is comparable with relatively high-precision methods of laboratory practice, and will provide a commercial tool capable of laboratory precision.

To illustrate the performance of the equipment, some films will be shown which were taken for Dr Allan Ferguson in connexion with his discourse on surface tension before the Royal Institution. One of the subjects under observation is the splash of a drop under varying conditions, and it is interesting to recall that Worthington in the latter part of the nineteenth century occupied himself for several years in obtaining, with the aid of a highly ingenious electro-photographic device, a series of instantaneous photographs illustrating the various phenomena. He produced some hundreds of excellent photographs, but since these are simply a selection of stills the interpretation of continuity is largely a function of the imagination of the observer.

The films taken of the same phenomena for Dr Ferguson were taken without any special preparations and the complete series was shot in three afternoon sessions of 2 hours each.

CONDENSED TABLES FOR COLOUR COMPUTATION

BY T. SMITH, M.A., F.INST.P., F.R.S.*

Addendum to discussion

Mr D. B. JUDD (Bureau of Standards, Washington, U.S.A.). I have two objections to the derivation of condensed tables according to the author's method. The first is that high-order Lagrangian interpolation is from a practical standpoint an unsuitable base from which to start the argument; the second is that it seems not to have been proved that the purely theoretical problem can be "solved by the construction of special tables."

In order to explain my first objection I refer to the second paragraph of the paper: "The formally correct procedure is then to measure at the 10-m μ . intervals, to interpolate values for the 5-m μ . intervals by a suitable formula, and then to compute exactly as though observations had been made at the 5-m μ . intervals." This would be correct if it had specified a suitable *method* instead of a suitable *formula*. I am not at all sure that there is any formula generally suited to interpolation of spectrophotometric data; and, in particular, I am very sure that Lagrangian interpolation of the 20th order is not suited to all cases.

As an example, the accompanying diagram shows the spectral transmission of Signal Red Glass No. 126†. The circles show the measured transmissions and the dots indicate values obtained from Lagrangian interpolation of the 20th order. The curve is drawn so as to pass through both circles and dots; hence it represents closely the result of Lagrangian interpolation of the 20th order. It is seen that this curve is not satisfactory; it descends to impossible values of less than zero by amounts that are significant. The graphical method of interpolation, on the other hand, would quickly yield much less objectionable values, because values less than zero could easily be excluded.

The statement, then, that an abridged table gives the same result as would be obtained by using high-order interpolation for obtaining intermediate values of spectral transmission is not always an argument in favour of its adoption; in some cases it is an argument to the contrary.

Before explaining my second objection I ought to state that I do not know whether the author's tables really fail to give 10-m μ . sums in agreement with the official 5-m μ . sums referred to transmission interpolated by a high-order Lagrangian formula; but I doubt if they do because the proof given is not complete. By writing out the expression (p. 375) completely it is seen that

$$\Sigma bc = \Sigma b'_0 c_0,$$

only provided

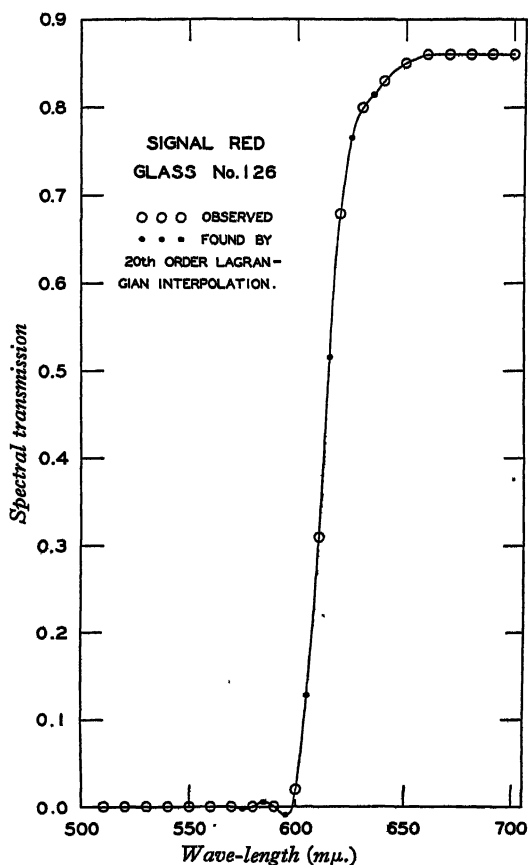
$$\Sigma b_e (\Sigma w_0 c_0) = \Sigma c_0 (\Sigma b_e w_0).$$

* *Proc. Phys. Soc.* 46, 372 (1934).

† *Proc. A. R. A. Signal Section*, 30, 407 (1933).

But this is not the case; the final sum is not independent of the order in which the operations are carried out.

This concludes my objections, but I have a final comment to make. If condensed tables are to differ at all from alternate entries of the official tables* my impression would be that an average value of the function for the interval should be given instead of the value at the middle of the interval. But the interesting result obtained by the author in his note on integrals of products of experimentally determined



An example of 20th-order Lagrangian interpolation of actual spectral-transmission data. It may be noted that the interpolation by formula is not admissible because it gives values less than zero.

magnitudes† goes far toward persuading me that the gain to be had, if any, is not worth the trouble. Our experience agrees perfectly with that at the National Physical Laboratory described by the author's statement: "In fact, the standard-observer properties are smooth enough for the outstanding irregularities to produce no difference that could be appreciated in any tests that have so far been made...."

AUTHOR'S reply. I should like to thank Mr Judd for sending a contribution to the discussion of my two papers. The points which he describes as objections are of

* As in *J. Opt. Soc. Am.* 23, 365 (1933).

† Page 365 of this volume.

interest, and I am glad to have the opportunity of saying a little about them. I have evidently given Mr Judd the impression that I regard 20th-order Lagrangian interpolation as a generally applicable method of interpolating among spectrophotometric measurements. This impression is quite incorrect. The 20th order was found to be sufficient for accurate interpolation to four figures of the Standard Observer tables, when the condensed tables were being constructed. I have nowhere stated what expression is necessary or sufficient for the properties of a source or material. If the purpose of the interpolation formula were to give a value for the intensity of the radiation at a particular wave-length, it is obvious that a formula giving negative values would fail, or alternatively that the observed points in the neighbourhood considered were not dense enough for the formula selected to be satisfactory. But the presence of negative values of the kind illustrated does not mean that the use of this formula would probably give rise to any detectable error in the integrals we are considering. It will be observed that the false negative value tends to be balanced by excess positive values immediately on either side. Phenomena of this kind are familiar in mathematics and mathematical physics. For example there are well-known expressions for evaluating areas in which negative weights are given to some ordinates: and the applications of Fourier's theorem constitute an important group in which we obtain correct results in spite of features of the type to which Mr Judd has called attention. I am unable to agree with Mr Judd's argument that a feature of this kind is a valid reason for not using the formula.

Mr Judd's second objection relates to the basis on which the tables have been computed. He says in fact that the work rests on a false assumption. I admit that the basis of the work was explained very briefly, but the error is certainly in Mr Judd's remark, and not in my work. Stated more fully the foundation is

$$\text{and} \quad \Sigma b_r c_r = \Sigma b_{2r} c_{2r} + \Sigma b_{2r+1} c_{2r+1}$$

$$\Sigma b_{2r+1} c_{2r+1} = \Sigma b_{2r+1} \{w_1 (c_{2r} + c_{2r+2}) + w_3 (c_{2r-2} + c_{2r+4}) + w_5 (c_{2r-4} + c_{2r+6}) + \dots\},$$

where the weights w_1, w_3, w_5 , are independent of the value of r and depend only on the differences of the suffixes of b and c . In this sum we have only a finite number of non-vanishing terms, and so we do not change the value by regrouping the terms. We may collect together the terms involving c_{2r} and obtain

$$\Sigma b_{2r+1} c_{2r+1} = \Sigma c_{2r} \{w_1 (b_{2r-1} + b_{2r+1}) + w_3 (b_{2r-3} + b_{2r+3}) + w_5 (b_{2r-5} + b_{2r+5}) + \dots\}$$

leading to

$$\Sigma b_r c_r = \Sigma b'_{2r} c_{2r},$$

where

$$b'_{2r} = b_{2r} + w_1 (b_{2r-1} + b_{2r+1}) + w_3 (b_{2r-3} + b_{2r+3}) + \dots$$

This is the result on which the calculations are based. It may be interpreted as showing what we ought to understand by Mr Judd's "average value of the function for the interval." It is this value which I have tabulated in the paper, and it is available for every one to use without any trouble at all.

I am glad to know that at the Bureau of Standards the Standard Observer tables have been found as satisfactory as regards smoothness as at the National Physical Laboratory.

REVIEWS OF BOOKS

Theoretical Physics, volume 2; *Electromagnetism and Optics*, by Prof. W. WILSON.
Pp. xi + 315. (London: Methuen & Co.) 18s. net.

Prof. Wilson's first volume*, *Mechanics and Heat*, has already made many friends, and the volume now appearing is assured in advance of a warm welcome. More than half is devoted to classical electromagnetic theory. This is followed by two valuable chapters on electron theory, a short chapter on geometrical optics, and just over fifty pages on some major topics in physical optics which have not already been dealt with as branches of electromagnetic theory. The volume concludes with a chapter on "General questions concerning the propagation of light," leading up to the discussion of relativity, which, with quantum dynamics, is to be the subject of the third volume.

The skill of the writer and the largely mathematical form of his argument have made it possible to compress into a remarkably small space a surprisingly comprehensive survey of classical and immediately pre-quantum (the use of this adjective seems unfortunately unavoidable) physics. This compression has not, however, been achieved at the expense of clarity of exposition; in fact, several points which usually present difficulties to students are here discussed much more fully than is usual in treatises of this scope. The problem of the variety of electrical units in common use, which is often, for beginners, elevated to the rank of a quite unnecessarily imposing bugaboo, is here handled in a thoroughly competent and sensible manner.

While the selection of the subject-matter has necessarily been along conventional lines, the treatment is both markedly individual and consistent. A particularly valuable feature is that, while presenting the classical physics, the author has his eye continually, if unobtrusively, focused upon the later developments of the subject; again and again, details of the older theory which are of special importance in more recent work are given special prominence. The reader who uses this book intelligently can scarcely fail to see "physical theory as a coherent logical unity." The author has earned the warmest thanks of all teachers and senior students of physics.

H. R. R.

Les Bases expérimentales immédiates de la Théorie des Quanta, by P. AUGER, E. BAUER, L. DE BROGLIE and M. COURTINES. Pp. 29. (Paris: Hermann et C^{ie}., 1933.) 10 fr. (paper covers).

This pamphlet is off-printed from the *Revue d'Électricité et de Mécanique*. E. Bauer contributes an historical introduction and an account of the Compton effect. P. Auger writes on the photoelectric effect, especially at X-ray frequencies, in gases, and M. Courtines describes experiments on the collisions (elastic, inelastic and superelastic) of electrons with gas molecules. The pamphlet concludes with a three-page summary by L. de Broglie on "quanta and wave mechanics."

The treatment, though authoritative, is elementary and non-mathematical, and the discussion is confined exclusively to quantum phenomena in which there is, at least superficially, immediate contact between theory and experiment. As in most French popular scientific writings, the style is very lucid.

H. R. R.

* Reviewed in *Proc. Phys. Soc.* 43, 458 (1931).

Introduction à la Théorie des Groupes et à ses applications à la Physique Quantique, by E. BAUER. Pp. 170. (Paris: Les Presses Universitaires de France.) 40 fr.

For some reason the explicit introduction of the theorems on groups of substitutions into modern quantum theory has called forth a number of books on the subject; the one now under review is more of a treatise on group theory than on quantum theory, and is presumably needed because physicists in general are not familiar with that subject. Let their mathematical teachers, then, take note of the point and see that it is introduced into students' curricula at an earlier stage!

After all, the ideas of group theory are interesting, easy to grasp and useful. The unification they introduce into the subject of differential equations was brought out by the work of Lie long ago, and was put into elementary form in the text book by Page.

As a matter of fact, the whole idea of substitution, and the equivalent idea of transformation, is central to mathematical theory. About half of Forsyth's great treatise on function theory is based on the idea of transformations. When transformation is linear in many variables, we represent it quite naturally by the matrix of the coefficients in the equations of transformation, so that the subject is also closely connected with algebra. Moreover, the multiplication theorem itself for matrices was devised to suit their application to the transformation of variables.

Another non-commutative algebra, the first discovered, is that of quaternions, and it too was based on the idea of transformations, the quaternion being an operator which turns one vector into another. Here we link the notions of geometry to analysis, a co-ordination which can be applied to transformations in general. When the variables are changed from the set (x_1, x_2, \dots) to the set (y_1, y_2, \dots) we can imagine them to be cartesian co-ordinates in space. The transformation then figures as a distortion (or remodelling) of the space. For example, if x_1, x_2 are cartesian co-ordinates in a plane, and y_1, y_2 are the polar co-ordinates, then by treating the latter as cartesian co-ordinates the circle $x_1^2 + x_2^2 = a^2$ is turned into the infinite strip $y_1 = \pm a$.

When the idea of geometry is linked to that of linear transformation, objects are moved without distortion (or with only simple strain), but there is a second interpretation of the same transformation. Instead of letting the body move, the axes of reference can do so. This duality in the conceptions appears trivial, but is of an importance which is well brought out in the book under notice.

The English student, if he does not study the original memoirs, has to find his group theory mainly in books devoted to algebra (Chrystal, Bôcher or Turnbull for example) and on differential equations (Ince or Page). A systematic survey of the subject is thus distinctly useful, and the present one, being in French, is easier for the average English reader than are those in German. It is marked by the characteristic lucidity and logical outlook of the French mathematician, and, curiously enough, is printed on good paper. Whilst containing no very recent results, it is more advanced as a treatise on group theory than the English authorities mentioned, and introduces most of the important general results in atomic physics, such as the theory of the Zeeman effect and of exchange degeneracy.

J. H. A.

Actualités Scientifiques et Industrielles, No. 74. *Spectres Moléculaires: Étude des Molécules Diatomiques*, by P. SWINGS. Pp. 52. (Paris: Hermann et C^{ie}, 1933.) 14 fr.

This recent addition to a well-known series of monographs may be regarded as a continuation of the preceding number (73) by the same author. This accounts for a somewhat abrupt opening, and for the facts that the first table is "Tableau VII" and the first three references are "Weizel, *loc. cit.*..." which is easily identified with *Banden-*

spektren (Leipzig, 1931). Many sections of the monograph, in fact, appear to be adaptations of the corresponding sections of Weizel's book. The subjects briefly discussed include the interactions of molecular rotation and electronic angular momenta, symmetry and anti-symmetry in rotational terms, isotope effect, selection rules for term combinations, structures of band-systems and of individual bands of several types, and fluorescence spectra. The selection of material and the treatment are very good, and the booklet should prove extremely useful to those readers, especially those French readers, who do not need the observational data, bibliographies and important details which are to be found in the larger English and German works on this subject. W. J.

Electromagnetic Waves, by F. W. G. WHITE. Pp. viii + 108. Methuen's Monographs on Physical Subjects. (London: Methuen & Co., 1934.) 3s.

In this little volume Dr White gives a clear and concise summary of the theory of electric waves, logical but without undue insistence on mathematical rigour, and with a discreet use of the methods of the vector calculus, which should prove of great service to a large number of physics students. The last chapter, on wireless waves in the earth's atmosphere, is an excellent and easy introduction to some of the beautiful work in this field which we owe to Prof. Appleton and his school. H. R. R.

Mass-spectra and Isotopes, by F. W. ASTON. Pp. xii + 248. (London: Edward Arnold & Co., 1933.) 15s. net.

Dr Aston's first book on *Isotopes* (1922) was mainly concerned with the remarkable and fundamentally important results which had just emerged from its author's beautiful work with the first mass-spectrograph. So definite and so complete within their prescribed limits were these first results that it became immediately evident that the next advance could only be made by still further increasing the accuracy of measurement of isotopic relative masses.

In the volume now under review Aston, who from the first appreciated the need for increased accuracy, gives the whole story of the development of the mass-spectrograph into an instrument of the highest precision. Side by side with the great technical difficulties of introducing the necessary refinements without too much loss of intensity, there have been other problems of a quite different kind but of a similar order of obduracy. These are the problems, very acute for many of the elements, of obtaining suitable beams of mass-rays and getting them into the spectrograph for analysis. The whole investigation is a model of skilled and tenacious experimenting, and it is admirably summarized in this volume; it says much for Dr Aston's power of description that he has been able to depict so many trees without ever obscuring the general view of the wood.

Parts 1 and 2 of the book give a full historical introduction to the whole subject and a detailed account of the work done with the mass-spectrograph and by Bainbridge with his apparatus. Part 3 summarizes our present knowledge of the isotopes of the elements, arranged in their groups. Part 4, "Theoretical and general," which terminates the book, has chapters on the electrical theory of matter, isotope statistics, isotope effects in molecular and atomic spectra (contributed by Dr C. P. Snow), and the separation of isotopes. Full use is made of illustrative diagrams, and the treatment is so clear that the book may quite well be recommended to beginners and to general readers, as well as to the specialists for whom it is indispensable. The appearance of this successor to the *Isotopes* is particularly timely, coming as it does when the events of the past two or three years have so insistently stressed the importance of its subject-matter throughout the whole domain of atomic and nuclear physics. H. R. R.

Faraday's Diary: being the Various Philosophical Notes of Experimental Investigation made by Michael Faraday, D.C.L., F.R.S., during the years 1820-62, volume 3 (May 26, 1836 to Nov. 9, 1839). Pp. xii + 466; volume 4 (Nov. 12, 1839 to June 26, 1847). Pp. xii + 448. (London: G. Bell & Sons.) To be completed in seven volumes. £12. 12s. the set.

Apart from the long period during which Faraday was debarred by serious ill health from all sustained experimental research, the record of these two volumes is one of inspired and conspicuously fruitful activity. In volume 3 we find the notes of the classical experiments on "specific inductive capacity," and while Faraday's methods and general results in this field are familiar to the youngest student of electricity, we are enormously enriched by this publication of the detailed notes. There is, of course (to take only one example), a strong interest for all working physicists in such experimental details as those of Faraday's struggles with leaky insulators and soaking dielectrics; what is, however, of the first importance is that we have here the full story of the unfolding of the conception of action through the medium—the "action of continuous particles affecting each other in turn, and not an action at a distance"—as the root cause of electrical phenomena. Nowhere else—not even in the *Experimental Researches*—can we find so perfect a picture of the development of the idea which directed the whole course of electrical theory in the later nineteenth century.

Again, in volume 4 we have the accounts of two further discoveries of fundamental importance—that of the magnetic rotation of light in the "heavy glass" and other media, and that of the universal nature of magnetism. It is worthy of note that these discoveries followed, in rapid succession, hard upon the period of enforced inactivity to which reference has already been made.

The importance of these three major electrical researches is too well known to need stressing, especially in these *Proceedings*. It may, however, not be without point to add that no one who reads the account of them in the *Diary* can fail to appreciate why (as we have it on record in Schuster's *Biographical Fragments*) the perusal of a notice of Faraday's work was sufficient to give to one acute and original mind its first impulsion towards physical science.

Of other notes in these two volumes, the more important series relate to work on the discharge through gases, on voltaic electricity, on the electrification produced by steam jets, and on the liquefaction of gases. In addition there are a number of illuminating speculative passages, disconnected notes on a variety of subjects, mainly electrical, and a detailed account of the experiments performed, with several voluntary assistants and one conscript (the "live gudgeon"), on the long-suffering gymnotus at the Adelaide Gallery.

It remains only to record that the editorship and production are of the high standard which characterized the first two volumes, and that the advent of the new volumes serves to enhance our sense of gratitude to the Managers of the Royal Institution for the service they are performing in giving the *Diary* to the world.

H. R. R.

Modern Thermodynamics by the Methods of Willard Gibbs, by E. A. GUGGENHEIM. Pp. xvi + 206. (London: Methuen & Co.) 10s. 6d. net.

It is probable that no more than a small proportion of the admirers of Gibbs's thermodynamical writings habitually use his methods as working tools for the solution of thermodynamical problems. Here, in a short and well-written treatise, Mr Guggenheim stresses the relations between the chemical potentials and other more recent concepts of physical chemistry, and he builds up logically and elegantly a system of thermodynamical relations which fully displays the utility and power of the methods first developed by Gibbs. His

treatment of the properties of solutions is particularly full, but in contrast with this he dismisses the "third law of thermodynamics" somewhat summarily.

The book should have a definite appeal both to physical chemists and to physicists. This appeal would have been stronger, especially to relatively inexperienced readers, if the author had relaxed the austerity of his design to the extent of including a few numerical examples, representative of the behaviour of actual substances and illustrative of the principles he expounds. If he really anticipates that his book will be read by those who are only "vaguely acquainted with the physical meaning of the first and second laws of thermodynamics," and "not necessarily with their applications" (*Preface*, p. viii), some such concession would clearly not be out of place.

Apart from this real, if minor, defect, the book can be warmly recommended to students of thermodynamics. It is original in design and treatment, and it makes an admirable supplement to the existing texts of a more conventional type.

H. R. R.

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FURTHER EXPERIMENTS IN ILLUSTRATION OF THE GREEN FLASH AT SUNSET

By LORD RAYLEIGH, F.R.S.

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ABSTRACT. An experimental imitation of the phenomenon of the green flash at sunset is described, an artificial source of light and a prism whose dispersion is equal to the atmospheric dispersion being used. A straight edge parallel to the base of the prism plays the part of the horizon. The observer was 74 metres from the prism. On moving the eye into the shadow of the straight edge, the bluish-green flash was well seen. Other experiments deal more specifically with the colour of the flash. By means of substantially the same arrangement with large dispersion and short distances the simultaneous-contrast effect of a red or orange background was studied, but it was not found possible to obtain a green as opposed to a blue flash in this way. If, however, a liquid containing small particles in suitable concentration is used in front of the source it is easy to make the disappearing flash of a brilliant green colour. The source viewed by transmission is then a pale orange. It is concluded that when the flash is bright green, atmospheric filtration is acting to remove the blue light. Contrast effects due to the red or orange colour of the sky do not seem to be important in this connexion.

§ 1. INTRODUCTION

THE green flash is seen under clear atmospheric conditions as a momentary appearance at the vanishing limb of the sun, when sunset occurs under a sea, desert, or mountain horizon*. It has of recent years been usually attributed to atmospheric dispersion, which would naturally keep the more refrangible part of the spectrum in view when the rest had vanished.

In a paper published in 1930† I discussed whether the normal atmospheric dispersion, calculated from the known refraction at the horizon ($35''$) and the known dispersion of air, was adequate in amount to produce this effect, and concluded that it *was* adequate. The essential point of the discussion is that the length of spectrum produced by the atmospheric prism varies as the direct distance of the horizon from the observer, whereas the linear size of the diffraction pattern, defining the diffuseness of the shadow, varies as the square root of the distance. Hence with increasing distance the conditions become increasingly favourable for observing a definite chromatic border at the edge of the shadow; at a distance of several miles

* General references are: A. A. Rambaut, *Symons' Meteorological Magazine*, 41, 23, 40 (1906); M. E. Mulder, *The Green Ray*, London, 1922; P. Feenstra Kuiper, *De Groene Strahl*, 1926.

† *Proc. R.S.* 126, 311 (1930).

the shadow is more than sharp enough to give the chromatic effects full scope. In other words the atmospheric spectroscope has adequate resolving power, its effective aperture being, not that of the eye, but a much larger aperture which may be considered as located at the horizon.

These conclusions were illustrated by means of a crown glass prism of angle $45'$ which, it was calculated, had the same dispersive power as the atmosphere near the horizon. A straight edge representing the horizon was placed across the aperture at the thick end and parallel to the base. When a beam of sunlight was admitted through this prism and received on a screen 20 metres away, the shadow cast by the edge was seen to be distinctly bordered with colour. The colour was described as greenish blue.

The present paper describes additional experiments intended to illustrate the green flash. They deal first with the imitation of the effect by means of a prism having dispersion equal to that of the atmosphere without special reference to the exact colour; and secondly with the imitation of those conditions which usually determine the colour to be green rather than blue.

§ 2. A MODIFIED EXPERIMENT IN IMITATION OF THE GREEN FLASH

The experiment described in the former paper and in the introduction, though conclusive enough as a verification, differs somewhat from the natural green flash in that the colour is observed on a screen rather than received direct into the eye. The direct light of the sun when high up is too bright for convenient observation, and moreover the fringe of colour at the available distance of 20 metres from the obscuring edge is too narrow to fill the pupil of the eye, and it becomes lost in the general glare. I have sought to modify the experiment so as to imitate more closely the natural effect.

To do this it is necessary to use longer distances than are available in the laboratory, and therefore to work out of doors. To avoid the excessive brightness of the high sun an artificial source was used. Since this is to be observed at a considerable distance it should have large linear dimensions, say $\frac{1}{100}$ of the distance from the observer, as is roughly the case with the sun.

A strip of opal glass, backed by a row of nine incandescent lamps, 25 watts each, was used. The lamps were in a box, with the opal strip let into the side. The strip was masked so as to present a luminous segment of about 3.4 metres radius, and to minimize false light it was eventually found necessary to supplement the mask by a second mask, so that the visible part of the opal was a circular arc*, 2 mm. broad, figure 1. The prism used to imitate atmospheric dispersion requires to have a long refracting edge, say half the length of the source or 50 cm. long. To avoid the expense and delay of having a special glass prism made, a water prism was assembled from plate-glass strips, measuring 50×7 cm. and 1 cm. thick. These were placed together at an acute angle with two of the long edges in contact and

* A narrow segment would represent the vanishing limb of the sun better than an arc of light, but in other respects is less convenient. The point is of secondary importance.

with slips of window glass to cover the side and bottom edges. The whole was assembled with Prout's elastic glue. This cement becomes viscous in a hot room, and it was possible to adjust the angle by the use of gentle mechanical force without taking the prism to pieces.

The refraction of the atmosphere at the horizontal is $35'$ and the relative dispersion $(\mu_F - \mu_G)/(\mu_D - 1)$ is 1.04×10^{-2} . In order that a water prism (with relative dispersion 1.8×10^{-2}) should be equivalent to this, its deviation should be $35' \times 1.04/1.8$ or $20'$. The water prism as set up gave a measured deviation of $21'$, which is a satisfactory approximation. Since the thick end of the prism was open, this end was necessarily uppermost, so that the whole arrangement was inverted as compared with the atmospheric refracting layer, and the light passed below the horizontal obscuring edge representing the horizon. This edge was, of course, placed so as to cut off the thick end of the prism. The source was 56 metres on one side of the prism, and the observer 74 metres on the other. When the eye was got



Figure 1.

into the right position, the source could be made to vanish behind the obscuring edge by a slight upward movement of the head and the greenish-blue disappearing flash could then be seen; or, by keeping the eye in an appropriate position, it could be held in view. If an ocular diaphragm was placed in the most favourable position, so that the colour was seen at the bottom (horizontal) position of the disappearing arc, then the colour at the bottom was lost in darkness if the diaphragm was raised 1 cm., and was lost in full illumination if it was lowered 1 cm. I myself was able to observe best with a Galilean telescope giving $\times 2$ magnification. My assistant, Mr R. Thompson, whose vision is unimpaired, preferred the naked eye*.

If the eye is lowered slightly from the position where the colour is seen at the bottom of the arc, the colour retreats towards the higher parts of the source on either side, the bottom being yellow or white by comparison. The two stages are roughly shown in figure 2, the shading indicating green. This effect is not so well



Figure 2.

seen with a luminous segment, like the setting sun, as with a luminous arc. In that case the glare due to the fully exposed segment is too great. In the present experiment it was found that to work with a full segment made the observations much less satisfactory, the aperture of the prism being filled with false (scattered) light when viewed from inside the shadow. This circumstance is instructive in connexion

* A small telescope is generally found advantageous for observing the natural green flash at sunset.

with the apparent caprice in the visibility of the natural green flash. A little false light due to atmospheric agencies is enough to obliterate it.

The experiment described seems to approach as nearly as could be wished to an artificial reproduction of the green flash, the question of the exact colour being left aside for a moment. Since the distances used are so very much smaller than those in the natural case, there appears to be no special point in reducing them still further except as a matter of practical convenience. It may be mentioned, however, that the colour could still be well seen when the distance from the prism to the observer was reduced to 36 metres.

The source limited to an arc 2 mm. wide, as described, may be considered to approximate to a spectroscopic slit, and on a first view of the matter it might be expected that a spectrum would be seen on looking at it through the clear aperture of the prism: or at any rate that one side would be visibly bordered by a blue-green fringe, and the other by a red. Such is not the case, and it is only when the obscuring edge at the prism is brought into action that the blue-green colour is seen. This circumstance illustrates very definitely the view briefly explained in the introduction, and more fully in the paper of 1930, that the adequacy of the resolving power essentially depends on the action of the horizon.

§ 3. THE CHROMATIC QUALITY OF THE FLASH

The view that the appearance of the green flash is due in one way or another to physiological contrast is an old one. The most obvious application of this idea is that it is merely the result of retinal fatigue. After the more or less reddish disc of the sun has been looked at, retinal fatigue shows a green appearance when this has vanished. The particular explanation called "successive contrast" is ruled out by the fact that the green flash appears at sunrise. Dr J. S. Haldane has, however, recently revived the same point of view in a different form*. He says: "Lord Rayleigh devised an experimental arrangement which enabled the effect to be studied at leisure. The colour seen was, however, blue, not green. It now seems evident, in view of the experiments described above, that the cause of the actual sunset or sunrise coloured ray being vividly green, is the simultaneous contrast effect due to the light coming from round the sun being red."

Dr Haldane has kindly informed me, however, in reply to a question, that like most recent writers, including myself, he regards atmospheric dispersion as the primary cause of the green flash. In his view simultaneous contrast comes in as a secondary cause to modify the subjective colour effect.

It is desirable to avoid any over-emphasis of the point to be explained. Although the colour is usually described as some variety of green such as bluish green, emerald green, or grass green, there are a number of records in the literature where blue is mentioned†. However, it is a fact that in most of the records green alone is mentioned.

* *J. Physiol.* 79, 129 (1933); *The Times*, June 10, 1933.

† For example: Lord Kelvin, *Nature*, 60, 411 (1899); E. H. Hills, *Monthly Note R.A.S.* 62, 430 (1902); Sir Flinders Petrie, *The Times*, June 3, 1933. In the latter two publications the blue phase is described as following the green at sunset or preceding it at sunrise.

We are not here concerned with the more general aspect of Haldane's investigation of the physiological significance of colour contrast, but I have repeated those of his experiments which seem to be most in point, and have found them interesting and instructive. The clearest form of experiment is to compare the effect of two coloured lights on a sheet of foolscap paper surrounded by black velvet; one half of the paper is illuminated by the first source and the other by the second source. The arrangement is simply that of Rumford's photometer: the black velvet eliminates any complication due to outer parts of the screen being illuminated by both sources. The most striking effects are obtained when the lights are of comparable intensity; this is secured by increasing the distance of the brighter light from the screen.

Dr Haldane finds that if one side is illuminated by a candle and the other by a red lamp, the former will appear a "deep green." I have myself been more successful in producing a green by using a daylight lamp as one source, and a red or orange lamp as the other. The daylight lamp gives white when used alone, but by contrast with the red or orange it appears what I should call a bluish green. This is the best success I have been able to get in producing by contrast a green from light that was not green by itself. I could not call it bright green, or grass green, or emerald green.

But, after all, the really relevant question is whether the blue of the spectrum can be made to look green by being contrasted with a red or orange light. To test this by Dr Haldane's methods, I used the blue radiation from a mercury vapour lamp with a suitable colour-filter to eliminate the green and yellow mercury lines, leaving the blue line $\lambda 4358$ virtually isolated. The blue patch from this was contrasted with a variety of orange and red sources with varied intensity, but neither my assistant Mr R. Thompson nor myself could describe it as anything but blue throughout*.

The above experiments did not give much reason to hope that the bluish flash could be turned into a green one by any method depending on colour contrast. But before abandoning the idea it was thought best to resort again to the direct method of experiment, prismatic dispersion being used to imitate atmospheric dispersion.

In experimenting on the purely chromatic aspect of the problem it is evidently unnecessary to use the rather arduous conditions of observation described in § 2. Ample prismatic dispersion may be used, which allows of short distances and a field of colour large enough for easy and convenient study in the laboratory. I have used a crown glass prism of angle 24° . This was set up in the same general manner, but the refracting edge was vertical, and, as before, an obscuring edge was placed over the thick end. An incandescent lamp with opal bulb served to represent the sun. The observer was 6 metres from the lamp with the prism half way. The general arrangement is shown in figure 3 (not drawn to scale). The disappearing flash seen with this arrangement as the eye moved into the shadow was of course dark blue

* I do not enter upon these more or less physiological questions without misgiving, bred partly of lack of familiarity with this field, and partly from dislike of the vagueness inherent in the use of words for describing subjective colour impression. It is certain that some people describe as blue what others describe as green.

or violet. The problem was to find what modification of conditions would make it a bright green.

I first tried whether a background of orange or red would produce this effect, as Dr Haldane has supposed might be the case. Various samples of red, orange and yellow cloth or paper were placed so as to be strongly illuminated by the lamp, and so as to form a background on which the disappearing flash could be seen. These coloured backgrounds could be alternated with white paper or with black velvet. The white or coloured background of course tended to make the blue flash less pure, but I could not by these methods get any approximation to green. The brightness of the background by this method was not under very convenient control.

An alternative method was to observe the disappearing flash against a self-luminous orange or red background formed by a second opal lamp with a coloured glass superposed. It was important so to tilt the coloured glass that the specular reflection of the main lamp in it was not visible at the point of observation. By controlling the voltage at the terminals of the second lamp the brightness of the coloured background could be controlled; but again I was not able to get anything but a blue disappearing flash.

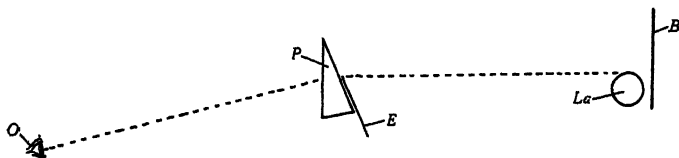


Figure 3. O, observer; P, prism; E, observing edge; La, lamp; B, coloured background.

Instead of coloured glass we may use as background the orange light transmitted through a scattering medium (rosin in water—see below) which approximates closely in physical causation to the orange colour of the sunset sky. This background was tried at various intensities, but again the flash remained blue and not green.

Thus in spite of persistent efforts no success has been obtained in reproducing the green colour by simultaneous contrast.

It has often been suggested that the green colour of the residual flash is to be explained by atmospheric scattering. Light from the low sun has to traverse a thick atmospheric layer, which preferentially scatters blue light laterally and transmits light of lower refrangibility, thus acting in effect as a yellow or orange filter which removes blue and leaves green as the most refrangible component of the spectrum. The scattering power of the atmosphere is variable according to the number and size of the dust particles present, and here we have the flexibility of conditions which is necessary to explain why the flash is usually described as green or blue-green, but occasionally as blue.

Pursuing the policy of experimental illustration, I have used a liquid scattering-medium in front of the source to represent the atmosphere. A metal tank 90 cm. long with glass ends was provided, large enough to transmit a beam of diameter 8 cm. This was set up next the source, between it and the prism, figure 4. It was filled with 7 litres of water, and a solution containing 1 gm. of rosin in 100 cm.³ of alcohol

was progressively added and well stirred in. This method of making a suspension of fine particles for scattering light is a very old one, originally due to Brücke*.

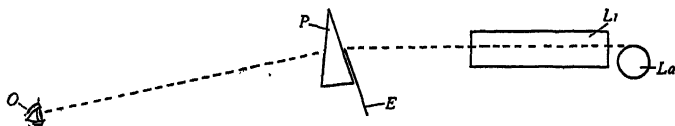


Figure 4. O, observer; P, prism; E, scattering edge; Li, scattering liquid; La, lamp.

With the gas-filled opal lamp at full voltage, the disappearing flash was observed. The results were as shown in the table.

Total quantity of solution added (cm ³)	Colour of lamp viewed through liquid without prism	Colour of disappearing flash
5	Pale yellow	Blue
10	Yellow	Bluish green
15	Pale orange	Full green (optimum)
20	Orange	Green, but diminished in intensity

The action of a scattering medium is thus well able to produce a full green colour in the disappearing flash.

The amount of scattering required is such as to make the source appear a pale orange. The setting sun is, of course, often seen blood red, so that the preferential scattering of blue light postulated is by no means excessive. Probably the green flash would not be seen with a blood-red sun; but so far as one can judge without the opportunity of observing in tropical seas, it would seem that this pale orange about represents the colour of the setting sun under conditions favourable for observing the green flash.

DISCUSSION

Instructor-Capt. T. Y. BAKER. The author has stated in this paper, and, I understand, in his previous paper of 1930, that the normal atmospheric dispersion calculated from the known refraction at the horizon (35') and the known dispersion of air, is adequate to produce the phenomenon of the green flash. If I understand his explanation correctly, it is based upon figures giving the refractive index of air for two colours, red and green. The values measured by Meggers and Peters† are: red 1.00029088, green 1.00029392. The dispersion of air, calculated like the dispersion of glass, gives a ν value of 96 just as a crown glass has a ν value of 60 and a flint glass one of 36. One could make a crown-glass prism with a deviation of 35', when the dispersion between red and green would be 35'/60 or 35"; or a flint prism

* *Pogg. Ann.* 88, 382 (1853). Brücke actually used mastic.

† Bureau of Standards, No. 327.

of the same deviation, when the dispersion would be $35'/36$ or $58''$. If one could make an air prism to give this deviation the dispersion would be $35'/96$ or $22''$, which corresponds roughly to some of the observed durations of the green flash when it has been seen. I gather that it is upon a calculation of this nature that the author bases his statement.

My objection to this explanation is that refraction through the atmosphere is different in its nature from refraction through a prism, and an explanation based upon measurements of refractive index and dispersion at sea-level densities alone is not adequate. Meggers and Peters's figures for red and green may possibly be questioned with reference to the last decimal place, but no one will dispute that the difference of three units in the sixth place does substantially represent the difference of refractive index for red and green light. It is a figure that is valid at any place on the earth's surface at any time. That being so, if the author's explanation is adequate the green flash should always be seen when the sun sets cleanly behind the horizon. Naturally one would expect small variations of the $22''$, but not variations amounting to complete elimination of the dispersion. And it must be remembered that the green flash is not a common phenomenon. It is the exception rather than the rule. From personal experience, although I have watched numerous sunsets and a few sunrises from the deck of a ship in the Mediterranean, I have never seen it there, and my first and only experience of it was at Southsea last year. On that occasion the duration was probably not more than $\frac{1}{2}$ sec., corresponding to $4''$ or $5''$.

The true explanation of the green flash is, in my opinion, much more complicated than the author suggests. Any consideration of astronomical refraction must necessarily be based on the assumption that the atmosphere is stratified in spherical layers concentric with the earth. In this non-homogeneous medium the path of a ray can be expressed in the form $np = \text{constant}$. That formula is to be found in many text-books, but perhaps the most appropriate reference I can give is Lord Rayleigh, *Phil. Mag.* 36, 141 (1893). In the formula n is the refractive index at any point of the medium and p the length of the perpendicular from the centre of the earth upon the tangent line to the ray at the point in question. The stratification being spherical, n is a function of height only, that is to say a function of r , the distance of the point from the centre of the earth. From the equation it is a simple matter to derive the value of ψ , the refraction of a ray which, entering the atmosphere from the outside, becomes tangential to the earth at sea level. Leaving out of account the additional refraction between the contact point and the observer's eye, the amount of the refraction up to the contact point is

$$\psi = \int_{r_0}^R \frac{n_0 r_0 (dn/dr) dr}{n \sqrt{(n^2 r^2 - n_0^2 r_0^2)}},$$

where n_0 is the refractive index at the earth's surface, r_0 the radius of the earth, and R the radius to the extreme limit of the atmosphere. The phenomenon of the green flash requires that integral to have a larger value for green light than for red. If one accepts $22''$ as being the average dispersion corresponding to the observed durations of the flash, then $\psi_{\text{green}} - \psi_{\text{red}} = 22''$. But it seems to me evident that

$\psi_{\text{green}} - \psi_{\text{red}}$ depends not only on $n_{0\text{green}}$ and $n_{0\text{red}}$, which is all that the author has taken into account, but on n_{green} and n_{red} for all heights.

The fact is that, although $n_{0\text{green}}$ and $n_{0\text{red}}$ do differ by 3 in the sixth place, and although n_{green} is greater than n_{red} at all heights, it does not follow that the magnitudes of the two integrals are necessarily different. For illustration only, and not as a suggestion of fact, we may take the case in which $n_{\text{green}} = kn_{\text{red}}$, where k is constant; it is obvious that in such an atmosphere ψ_{green} would be exactly equal to ψ_{red} . That atmosphere would be achromatic. No green flash could be seen. There are countless ways in which n_{green} and n_{red} could be made to vary with height (even with the restriction that n_{green} must be greater than n_{red} for all heights) while still satisfying the condition of achromatism. One has only to look at the form of the integral to see that a change of only a few units in the ninth decimal place for the bottom layers of the atmosphere (say up to 200 feet) is sufficient to alter the value of the integral by 20". In fact the differential changes between n_{green} and n_{red} that will change the condition of achromatism, where there is no green flash, into one favourable to the green flash, involve the remoter decimal places of the refractive index that are beyond the reach of direct measurement.

I suggest that whereas the author's explanation fails to account for the occasions when there is no green flash, the alternative outlined above does at least allow for all possibilities. If the normal condition is for the green flash to be an infrequent phenomenon, the conclusion must be drawn that the atmosphere is normally achromatic. The rarer occasions when the green flash is seen are departures from the normal. I am almost tempted to go further and suggest that the abnormalities conducive to the green flash are most probably found in the lower levels of the atmosphere. That is a conjecture that could be verified only if the refractive index could be measured with a much higher order of accuracy than is at present attainable. But in support, though not in proof, of my contention I would like to refer to measurements of the dip of the sea horizon made by ships of the Navy a few years ago. In this case abnormalities of the dip were entirely due to an abnormal condition of an extremely small part of the atmosphere, some seven or eight miles horizontally and 50 or 60 feet vertically. The normal condition of the atmosphere shows that a ray, nearly horizontal, has a curvature of about 8" per mile. Our measurements of the dip, some three thousand in all, showed variations between 32" and - 17" per mile. If there are these wide variations in dn/dh , which is proportional to the curvature, is it not extremely likely that there may be differences between n_{green} and n_{red} in these lower levels sufficient to account for a green flash?

Mr W. H. WHITE. I watch for the green flash in clear sunsets, in the mid-field of $\times 8$ Zeiss binoculars, and of course avoid staring at the sun beforehand. On one exceptional September day, intensely clear from the previous sunset (green flash) in the Channel, the broken flakes of the setting sun in Essex showed yellow-green upper margins: all other observations have been at sea (where it would be more generally seen of men if sunset were not usually during dinner) though a small

distant island was once no hindrance. Afternoon visibility must have been perfect, and the sun must begin to set with sharp outline, and without dulling to redness at the lower limb. A red sun, though it may spread at the last 3 or 4 sec. into a short line of liquid light, does not change colour. Change of colour begins at the horns of the thin segment, and moves inwards; it may be detectable 15 sec. in advance. A full orange sun goes pallid, and very briefly yellowish green; a yellow sun soon shows green edges and turns green to signal-green for 2 sec., or perhaps momentarily blue. With a bright, very slightly tinted, sun one may expect blue. In any case, the flash is many times brighter than the background of sky; and I have not noticed this ever producing complementary-colour illusions with white spars or the like. My last two observations were as follows:

(i) 1933/8/11, 33° N., 42° W. (400 miles S.W. Azores) ending a halcyon day of brilliance and calm, marvellously glassy blue sea. Green flash, turning blue, seen from foredeck (20 ft.) and exactly repeated from fore-castle deck, 9 ft. higher, 10 sec. later; a longer interval than simple theory suggests. Sky not notably coloured (clear night, abundant shooting stars).

(ii) 1933/9/7, 26° 30' N., 68° W. (300 miles S.W. Bermuda) moderate East wind, sea, and swell; western sky a broad blaze of bright gold, sun scarcely tinted. Green instantly turned blue, and lay as a liquid F line, persisting 5 sec. Not repeated on fore-castle later. The air may have been slightly less warm than the sea.

Instructor-Lieut. D. K. McCLEERY. I should like to ask the author whether he can account for the fact that the phenomenon is much more frequently seen in the tropics than in higher latitudes. I have seen the flash in latitude 45° N. in the western Atlantic and it was a very brilliant one. There was on this occasion a double flash owing to the fact that I was standing in the bows and the ship was pitching to a W.S.W. swell. The temperatures of the air and sea were alike 56° F.; I mention this fact to show that there could not have been any abnormal refraction. It would be a good thing if observers could record the temperatures at sunset; they can easily be obtained from the ship's log.

The rate of setting of the sun is easily shown to be $15 \sqrt{(\cos^2 \text{lat.} - \sin^2 \text{dec.})}$ seconds of arc per second of time, which means a rate of about 6 to 9 in our latitudes.

The conclusion at the end of the paper that "probably the green flash would not be seen with a blood-red sun" seems to be well borne out by experience. I have looked for the flash hundreds of times but have never seen it with a red sun.

Dr W. D. WRIGHT. I have made a large number of experiments recently on the effect of successive contrast in changing the appearance of various colours and in no case has it been possible to change a blue into a green, provided that the blue has been reasonably pure and not a blue-green. The correct explanation of this is, apparently, that blue is one of the fundamental responses according to the trichromatic theory of colour vision, so that even if a deep violet radiation were available to produce the contrast, blue could still not be converted into green. Moreover the effects of successive contrast are very much stronger than the similar effects of

simultaneous contrast, so that I do not think there is any doubt that the cause of the flash appearing green instead of blue is physical rather than physiological.

Mr A. F. DUFTON. In his introductory remarks the author referred to the green flash as a somewhat rare phenomenon. There is another phenomenon which is proverbially rarer still, the blue moon. Until this afternoon I did not realize that the moon could appear blue, but an hour ago I had occasion to refer to *Nature* for 1883 and found there an account of the green sun which in September 1883 was seen at places as wide apart as Madras, Trinidad and Ceylon. The account from Ceylon is interesting: "The sun for the last four days rises in splendid green when visible, i.e. about 10° from the horizon. As he advances he assumes a beautiful blue, and as he comes from this on looks a brilliant blue resembling burning sulphur. . . . Even at the very zenith the light is blue. . . . As he declines the sun assumes the same changes but vice versa. . . ." The account goes on to state that the moon behaved in similar manner. The phenomena were attributed to the eruption in Java.

Mr J. GUILD. The evidence given in the paper leaves no doubt in the minds of physicists that scattering is adequate to account for the green colour of the flash. Prof. Haldane, whose views are quoted in the paper, appears to over-stress the importance of simultaneous contrast in determining the colour quality of visual sensations, and to leave out of account many other important factors. As a matter of fact it is obvious on quite general principles that the change from spectral blue to green cannot be due to simultaneous contrast. The contrasting colour would have to be of still shorter dominant wave-length and of extremely high intensity. No conditions at all resembling this exist in the present problem.

Mr T. C. SUTTON. My remarks concern merely the ease with which the green flash may be seen. Under suitable conditions, this can be done more frequently than some of the speakers suppose. Some years ago I was in latitude 40° S.; the house faced due west, 200 ft. above an ancient lake bed, now a fertile but dusty plain. A phenomenon which I believe to be this flash was seen with perhaps 60 per cent of the sunsets. It was not always green; it might be any shade between orange and blue, but not red. The atmosphere was usually dust-laden. After rain the sky was very blue, and the effect was then seldom, I think never, observed. During one visit to this house, soon after or at the time of the eruption of Ngauruhoe 2000 miles due east, many strange sights appeared, among them the blue moon which has been referred to. It is perhaps worth notice that, while dusty summer atmospheres tended to make the moon appear orange, the higher and finer volcanic dust turned it a pale but brilliant blue-green.

Mr W. F. FLOYD. I should like to ask whether the spectral distribution of the light from the lamp used in the experiments described in § 3 of the paper approximates closely to that of sunlight at sunset on occasions which seem to be favourable to the appearance of the green flash; and further what is the order of the ratio of the absolute intensities of the light reaching the observer's eye in the experimental and in the natural phenomena. I am willing to accept a purely physical explanation

of the green flash, but I would suggest that the present paper establishes only one possible explanation. That a physiological effect may contribute to the phenomenon, or may even provide the sole explanation of it, has not been disproved, nor can it be disproved by purely physical arguments. As a contribution to the evidence that has been offered in the discussion, I would submit the following account of a personal experience. I have often looked towards the early morning sun from my window. If, having done so, I look on to a neutral background, or a coloured but not well illuminated background, I see an image of the window, the window space being full green in colour and the surrounding ground dark. I am able to see a similar image by closing my eyes and shielding them from direct light from the window, but in this case more detail is discernible, the image of the window space being fringed with blue-violet or violet. The succeeding events, while not bearing directly on the present discussion, are of interest. I find that with the eyes closed I can hold the image for several minutes by controlling the intensity of the light falling on the closed eyes, and also that the image colours change slowly down the spectrum. Later in the day I have found that the full green stage was preceded by a pale blue stage.

AUTHOR'S reply. So far as I understand Captain Baker's point of view, he thinks that the calculation of atmospheric dispersion given cannot be correct, because it proves too much; if it were correct, the green flash would always be seen, whereas it is in fact only rarely seen in most places. Most previous writers have felt more difficulty in satisfying themselves that the dispersion is enough. Captain Baker gives reasons which lead him to think that the atmospheric refraction may be of an achromatic character, but I do not clearly understand how achromatism can be got out of a single refracting medium: unless indeed variations of composition of the air are relied on, and I doubt if they can be stretched far enough.

But the whole difficulty seems to me illusory. False light in one form or another is an amply sufficient explanation of the cases in which green flash is not observed. In my experiments with the water prism I found it most necessary to take every precaution against false light, and Nature takes no such precaution.

In reply to Mr McCleery: I have always supposed that the comparatively common occurrence of the green flash in the tropics is to be attributed to the clearness of the horizon at sunset. The same would apply particularly to a desert horizon, and judging from the experience of one or two archaeologists who have lived in the desert for long periods, the green flash is a common occurrence there.

In reply to Mr Dufton: The blue sun seen under certain conditions is of great interest, but I am not able to throw any light upon it.

In reply to Mr Floyd: The lamp used was of the same order of intensity as the setting sun; but, in the absence of a scattering medium, it was bluer than the setting sun usually is. With the scattering medium, the colour passed through the various shades observed in the setting sun on different occasions.

AN ULTRA-VIOLET PHOTOELECTRIC SPECTROPHOTOMETER

By D. H. FOLLETT, M.A., A.Inst.P., Adam Hilger, Ltd.

Communicated by F. Twyman, F.R.S., December 22, 1933. Read April 20, 1934.

ABSTRACT. An instrument designed for accurate spectrophotometry is described. The transmission of the sample is found by comparison with a rotating sector, which is of cylindrical type and meets the criticisms usually directed against sectors whose transmission can be varied while they are running. Two photocells are employed and fluctuations in the intensity of the source are compensated for. The possible sources of error and their elimination are discussed and the results of tests are given.

§ 1. GENERAL CONSIDERATIONS

IN certain applications of spectrophotometry the use of photoelectric methods is definitely preferable to the use of photographic methods⁽¹⁾. No great confidence is felt, however, in photoelectric methods in general, as their absolute accuracy is often in question although they may be highly sensitive. In the instrument here described special attention has been given to the question of accuracy as distinct from sensitivity, and we consider that all the predictable causes of error have been avoided. Nevertheless, we are well aware that theoretical considerations are of limited value in appraising the worth of any photoelectric arrangement and that the only true test is that of comparison with other well-tried methods.

The use of gas-filled photoelectric cells is more or less essential owing to the necessity for obtaining a high sensitivity. This immediately precludes the use of any method in which the photocell is used actually to measure the intensity on the assumption of a linear relation between current and intensity. Spectrophotometric methods have been described in which this relation is assumed for gas-filled cells, and for which the authors claim that accurate results are yielded. They may have been fortunate in obtaining such cells, however, and it seems better to avoid such an assumption if possible.

As ultra-violet sources are most conveniently run from the mains supply, it is necessary to use some method in which fluctuations in intensity can be compensated for; this would probably be necessary even if the electric supply were perfectly steady. Smith and Holiday⁽²⁾ have described how they stabilized the output from a hydrogen tube, but as perfect stabilization cannot be obtained it seems desirable, since the highest accuracy is aimed at, to use a method which compensates for fluctuations even when a stabilizing device is used.

The method finally adopted is a modification of one which has been described by von Halban and Ebert⁽³⁾ and has been shown by von Halban and Eisenbrand⁽⁴⁾

to give results agreeing closely with those given by various photographic methods. The fact that their arrangement gave accurate results does not, of course, provide any guarantee that the present instrument will do likewise, but it indicates that there is no fundamental reason to the contrary.

§ 2. MEANS OF VARYING LIGHT INTENSITY

It is necessary to have a means of varying light intensity in a known way, and we have used a rotating sector for this purpose. The validity of Talbot's law for photoelectric cells has been questioned by some workers, but opinion seems fairly unanimous in its favour in England⁽⁵⁾. A more serious difficulty in the use of sectors is that they should be adjustable when actually running, and that owing to wear in the rather complicated mechanical arrangements by which this is achieved loss of calibration soon occurs. We have avoided this difficulty by using a sector of a new type described by Dunn⁽⁶⁾. This consists of a cylinder, rotatable about its

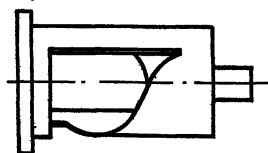


Figure 1 (a).

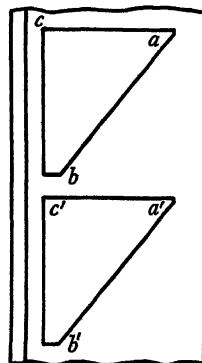


Figure 1 (b).

axis, with two apertures cut in its surface. These apertures are similar, and are bounded on one side by a straight spiral cut round the surface, and on the other by an edge parallel to the axis of the cylinder. Figure 1 (a) shows the sector, and figure 1 (b) shows the surface developed to a plane. ab , $a'b'$ are the spiral edges and ac , $a'c'$ the edges parallel to the axis. A beam of light passing along the axis of the cylinder is reflected radially by a right-angle prism. The cylinder is movable along its axis, and as it rotates, the light alternately passes through the aperture and is obstructed by the wall. The fraction of a revolution during which the light is transmitted depends upon the position of the sector with respect to the deflected beam. When the cylinder is moved along its axis the change in the fraction transmitted obviously varies linearly with the amount of movement.

§ 3. PRINCIPLE OF THE METHOD

Figure 2 indicates diagrammatically the optical system of the photoelectric arrangements. The lens B collimates the beam after it emerges from the slit S of the monochromator. The quartz plate H reflects a fraction of the beam into a photocell

L' , and the rest of the beam passes through the absorption tube C containing the sample. Lens K then focuses the beam, after reflection by the prism P , so that an image of the slit is formed on the wall of the sector. The light then passes into the photocell F . The photocells are connected so that they deliver currents of opposite sign to a Lindemann electrometer. The potentials on the cells are so adjusted that, with the sector running in its fully open position, these currents are exactly equal so that the electrometer does not charge up. The absorption cell C is then slid out of the beam and replaced by a comparison cell C_1 (e.g. one containing the solvent). The circuit is then re-balanced by adjusting the position of the sector. The photocell F is now receiving the same amount of light as before, and the ratio of the transmissions of the sector in the two settings gives the ratio of the transmissions of the two absorption cells C and C_1 . No relationship between current and intensity is assumed. Since both photocells are illuminated by monochromatic light, any variation in the intensity of the source will not affect the balance provided that both cells have the same (intensity, current) characteristic. This condition will be closely fulfilled over the small range of intensities in which fluctuations are likely to occur.

§ 4. OTHER METHODS CONSIDERED

Since the production of this instrument a description has been published of an arrangement which might be equally satisfactory⁽⁷⁾. A vacuum cell is used, and the linear relation between current and intensity is assumed. As no sectors are used, the new electrometer valve is employed to indicate null points. This is probably capable of higher sensitivity than the Lindemann electrometer, but the method entails the use of a high-resistance potentiometer ($10^8 \Omega$ in the arrangement described) and the sensitivity depends upon the value of this resistance. There are obvious difficulties in the manufacture of a high-resistance potentiometer, and it is probable that $10^8 \Omega$ is about the highest that can be used. Under these conditions the sensitivity is little, if any, greater than that of the Lindemann electrometer. The use of the gas-filled cell, possible in our method, thus seems to give a definitely higher sensitivity.

Another method of compensating for fluctuations in the light-source is that described variously by Hardy⁽⁸⁾, Dobson and Perfect⁽⁹⁾ and others. The beam emerging from the monochromator passes alternately through the sample and through a device for varying the intensity, the frequency of the alternation being from 10 to 50 times a second. The light falls on a photocell so coupled to an amplifier that only fluctuating currents are transmitted. If the two beams are not equal the light falling on the cell will be flickering, so that the amplifier gives an output, and the variable beam is adjusted until the amplifier shows no output. This method sounds very simple and large fluctuations of intensity in the original beam can be dealt with, provided that their period is large compared with that of the alternations. For ultra-violet work the chief difficulty in applying the method lies in finding a suitable means of varying the intensity of the comparison beam in a known manner; the rotating sector in some form, or a variable aperture, are the

only two feasible means in general, and of these the former is inapplicable to this particular case. The latter is always difficult to apply in photoelectric apparatus because an image of the monochromator slit has to be formed on the surface of the cell; quite slight aberration will cause variation in the size of this fine image for different apertures, and unless the sensitivity of the cell surface is completely uniform error is introduced in this manner.

§ 5. INSTRUMENTAL DETAILS

The lenses *B* and *K*, figure 2, are of quartz and it is therefore necessary that a focusing movement should be provided; knobs working over engraved scales are supplied for this purpose. The absorption tubes are mounted on a slide and are pushed alternately into the beam by means of a further knob. The photocells are Osram UNG 7, which is gas-filled and has a sodium cathode and quartz windows. The electrometer is read by means of a microscope and is illuminated by a lamp mounted outside the case; it is of the Lindemann type made by the Cambridge

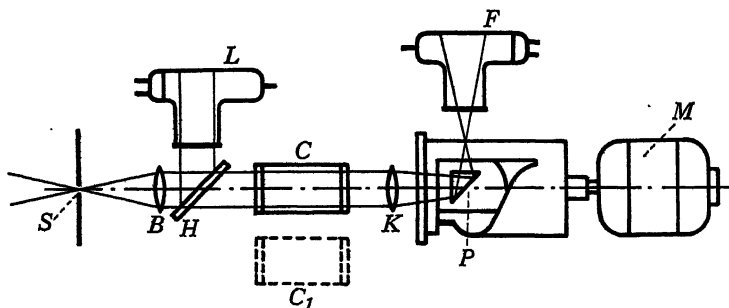


Figure 2.

Instrument Company, Ltd., and is chosen for its robustness and quick period. The earthing-switch is built into the electrometer and is operated pneumatically by means of a rubber bulb. The resistances used are ordinary commercial wireless components; we have used these for two or three years now and have never encountered any trouble which could be traced to them.

The sector itself is a cylinder 3 in. in diameter and the spirals are of 6-in. pitch. The closed end *a* does not go completely to a point, but has an aperture of about $\frac{1}{30}$ of the value of that at the open end *c*. It is mounted directly on the shaft of a motor *M*, which was specially selected to have no end play and to run without vibration. The only suitable motor which we could find is an Italian one, made by the firm of Marelli. It is mounted on a carriage which slides along the optical axis of the system, and is moved by a heavy screw of $1\frac{1}{2}$ mm. pitch, which enables the movement to be measured. The number of complete turns of the screw is registered by a revolution-counter, and the additional fraction of a turn is read by means of the graduations on the edge of a drum.

The photoelectric circuit is shown in figure 3. The resistances R_1 , R_2 , G_1 , G_2 are the usual protective resistances for the photocells and the electrometer re-

spectively. A_1 and A_2 are the potentiometers which vary the potentials on the cells; B_1 and B_2 are the potentiometers which vary the potentials on the plates of the electrometer. The circuit differs slightly from the orthodox circuit in that no connexion is made from the point E to earth. The current through the potentiometers B_1 and B_2 is then the same, and any variation in the batteries does not affect the ratio of the potentials on the two plates. This is the condition that the electrical zero shall remain constant⁽¹⁰⁾. If E is connected to earth, a change in the battery F , for example, will alter the potential on one plate only, so that the electrical zero will alter. It is important in this instrument that no changes of zero should occur while the two settings constituting one reading are being made. A similar arrangement is made for the potentiometers controlling the potentials on the two photocells.

The change δA in aperture produced when the sector is moved a distance d is given by $\delta A = kd$, where k depends on the pitch of the spiral. The distance d can be found from the indication of the revolution-counter and the drum. However,

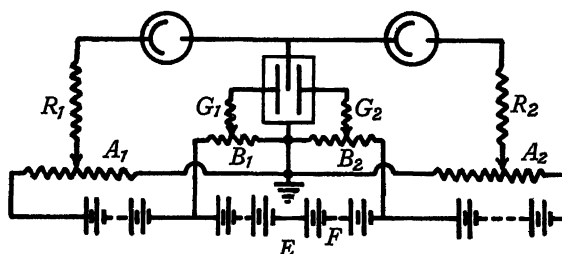


Figure 3.

the actual aperture of the sector must be known, since the ratio of the apertures at which balance is obtained for both sample cell and comparison cell must be found. The actual aperture is given by the relation $A = kd + P$, if d is the reading of the position of the drum and P is a constant which is the reading for the position at which the aperture would be zero if the sector closed down to a point at a , figure 1 (b). The value of k is easily calculated from the pitch of the spiral. P is most easily found as follows. A measurement is taken of the absorption of any convenient sample at any wave-length. Suppose A_1 and A_2 are the apertures of the sector at the two balance points. Then another reading is taken, this time with the apertures approximately half what they were before. If d_1 , d_2 and d_1' , d_2' are the respective readings of the position of the sector, then

$$\frac{A_1}{A_2} = \frac{kd_1 + P}{kd_2 + P} = \frac{kd_1' + P}{kd_2' + P}.$$

k being known, P can then be calculated.

§ 6. POSSIBLE SOURCES OF ERROR

The most obvious source of error was in the determination of the constants of the sector. If the constant P is zero, the value of k is immaterial. P can be made very small by suitably setting the revolution-counter, and the value of k

can be calculated with sufficient accuracy from the pitch of the spiral. In this instrument we thought it advisable to measure the aperture independently, and this measurement was carried out in the following way.

A beam of light from a motor head lamp was passed through the sector, and then through a radial sector and into a photocell connected to a galvanometer. The cylindrical sector was held stationary so that light passed through it uninterrupted, and the radial sector was rotated. The deflection of the galvanometer was noted, and then the sector was stopped. The radial sector was then set so that light passed through it uninterrupted; the cylindrical sector was set rotating and its position was adjusted until the galvanometer gave the same deflection as before. The angular aperture of the radial sector was measured carefully to about 5". The position of the cylindrical sector was plotted against the aperture of the radial sector, and the gradient of the plotted line was determined. It was found to be 0.125 radian per turn of the screw, whereas calculation from the ostensible pitch of 6 in. gives 0.124 radian per turn. This difference of nearly 1 per cent may arise in the setting up of the machine for cutting the spiral, or owing to the straight lines ac , $a'c'$, figure 1, not being cut exactly parallel to the axis of the cylinder.

Further experiments were carried out to test the uniformity of the curved edges of the sector. A mirror was fixed to the surface of the sector with wax, and a beam of light was reflected from it to a scale at a distance of 1 m. A microscope was then focused on the spiral edge and the position of the sector was set so that the edge came on to the cross webs. The sector was traversed a short distance, and then rotated until the edge came again on to the cross webs in the microscope. The movement of the beam on the scale was measured, a number of readings were taken and the scale readings plotted against the movement of the sector. Only a small section of the sector could be dealt with in one run of readings, otherwise the deflection became too big. Small local irregularities were found, but were completely negligible except perhaps at the narrow end of the sector. The magnitude of these random errors is never more than 0.0019 radian, and the smallest possible angular aperture is 0.200 radian for one aperture, corresponding to a transmission of nearly 7 per cent. Thus, even if one of these random errors occurs in the same direction in each aperture at any one setting of the drum, the error cannot be more than 1 per cent. For higher settings the error is proportionately less.

The error due to inaccuracy in the value of P , in the expression for the aperture, is not reduced by making P small, since P can be determined only to within certain limits which are independent of its actual value. Nevertheless, it is an advantage, as has been stated above, to make P small in order to increase the tolerance in k .

Error in positioning is avoided by joining the photometer to the monochromator by means of a ball-and-socket arrangement in virtue of which the photometer can rotate slightly, in a horizontal plane, about the exit slit of the monochromator when the two instruments are joined up. The exact adjustment is not critical and is made very simply as follows.

Figure 4 represents the optical system. An image I of the slit S of the monochromator is formed on the surface of the sector. The only possible displacement

of the photometer is a slight rotation about S , and the effect of such rotation is to cause the radiation leaving the slit to enter the photometer obliquely. The dotted lines represent rays so entering. If aberrations are absent, the image I is, of course, formed in the same place on the sector regardless of the angle these rays make with the axis, the only effect being a loss of light. The lining up is therefore not critical and is obtained very simply by slipping a tube over the end of the mount of the lens K . On the end of the tube are engraved a pair of parallel lines equidistant from the axis, and the instrument is rotated until the beam falls centrally between them.

The lenses B and K have a focusing motion along the axis. It is very desirable that they should be so mounted that the motion is accurately along the axis. If it is not so, there will be a displacement of the image I as the lens moves. Thus the value of the constant P in the expression for the aperture will be different for different wave-lengths. This is undesirable, although the value of P could be found for all wave-lengths, since it would entail additional calibration. The presence of the defect was looked for by focusing a microscope on the image I , and observing whether this moved as the wave-length of the monochromator radiation was changed and the lenses D and C were focused.

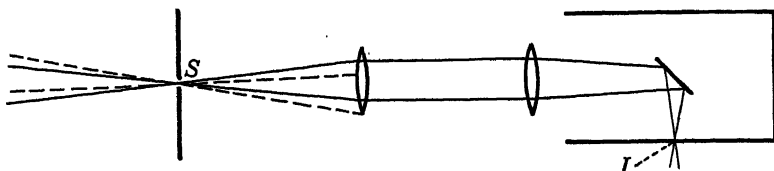


Figure 4.

Another possible source of slight error exists, though it is rather obscure. The width of the image on the sector is finite, so that the aperture of the sector varies across the slit. Let figure 5 represent the image of the slit on the sector. Let the line ef be such that the effective aperture of the sector is the same along the whole length of it, and let gh be a line parallel to it and distant s from it. Let the intensity be uniform along it and equal to I . Then it can easily be shown that the line fe represents the effective position of the whole image on the sector if $\Sigma Is = 0$. Obviously for a rectangular image uniformly illuminated, the effective position is the line dividing it into two geometrical halves. In practice, however, the image will not be so simple as this. The monochromator used with the photometer was the Müller-Hilger double monochromator. The front slit of this is curved, the curvature being such that a line of wave-length 3000 Å. gives a straight image at the slit which divides the two monochromating systems. This slit is straight. For any other wave-length the image at the slit will be slightly curved. To illustrate the point we may refer to figure 6. j represents the shape of the first slit. The full lines in k represent the shape of the image after dispersion in the first system. The dotted lines represent the boundaries of the slit, which cuts off a small portion of the image, as can be seen so that the shape becomes that shown at l . After dispersion by the second system the shape becomes as shown at m . The left-hand edge will fit the curved exit slit, but the right-hand will not. The difference between the shape

of the slit and that of the image will be different for different wave-lengths, so that in effect the value of the constant P will depend upon the wave-length. The extent of the effect will depend upon the length of the slit and can be reduced to negligible proportions by confining the illumination to the centre of the slit. With a continuous spectrum the effect practically disappears, because the space between the full and dotted lines (representing the left-hand edge of the slit) in m will be filled in. Thus the whole width of the slit will be illuminated, and the departure from uniformity of illumination will be very small except in exceptional cases where the absorption band is so steep that there is a marked change in absorption for the wave-length within the range which the slit covers. In this case there will be error due to the finite width of the monochromator slits in any case.

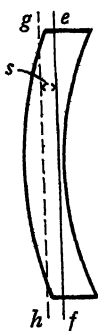


Figure 5.

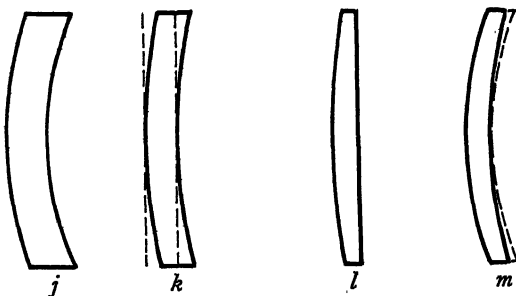


Figure 6.

§ 7. TESTS

To see if there were any systematic errors inherent in the instrument the transmissions of two pieces of optically worked neutral glass were separately measured, and then the two glasses were put together and the transmission of the pair was measured. The results are given below. Each measurement is the mean of several readings. Each figure is given to 4 places, though the significance of the fourth figure is very doubtful.

Transmission of first sample	0.2749.
Transmission of second sample	0.2746.
Calculated transmission of the two together	0.07548.
Observed transmission of the two together	0.07558.

The difference between the observed and calculated values is 0.13 per cent of their value.

The pieces of glass here used had been measured by the National Physical Laboratory at wave-length 0.5461μ . We have measured one piece at this wave-length and find an excellent agreement. The National Physical Laboratory figure for the transmission is 0.2985, while our instrument gives 0.2981.

§ 8. ACKNOWLEDGMENTS

Acknowledgments are due to Messrs Adam Hilger Ltd., at whose suggestion the paper is published; to Mr F. Twyman, F.R.S., and Dr F. Simeon who have contributed advice and suggestions; and to my assistants Mr W. J. McCarthy and Mr R. A. C. Isbell who have performed most of the experimental work in the development of the instrument.

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DISCUSSION

Mr J. GUILD. Much attention has been devoted to the design of photoelectric spectrophotometers in recent years, and extravagant claims have been made for their performance which, on examination, have usually been found to be quite baseless. The sources of possible systematic error in such apparatus are often very difficult to spot on theoretical grounds, and for this reason I never, nowadays, judge of the merits of an instrument of this kind from consideration of the design, but only from the results of critical comparisons with other instruments of known reliability. I could have wished, therefore, that the author had included more experimental results. However, in giving two he has given two more than is usual, and the results of these two certainly suggest that the present apparatus is not only sensitive but, what is much more important, accurate.

Mr T. SMITH. It is of interest to examine the test mentioned by the author in which the transmissions of filters together and independently are compared. The filters should of course be definitely separated from one another, and we may assume that they are placed normal to a parallel beam of light. The mutual effects of a single filter and the instrument should differ very little from those of two filters, and we can, therefore, consider two filters alone as an absorbing system.

Assume that reflection takes place only at the surfaces of the filters, and that in the body of the filter only absorption occurs. Then if P and N denote the amounts

of light travelling in the positive and negative directions on the incident side of one filter, and P' and N' are the corresponding quantities on the emergent side, we have

$$(PN) = (P'N') m,$$

where

$$m = \begin{pmatrix} 1 + \rho & \rho \\ -\rho & 1 - \rho \end{pmatrix} \begin{pmatrix} \frac{1}{\tau} & . \\ . & \tau \end{pmatrix} \begin{pmatrix} 1 + \rho & \rho \\ -\rho & 1 - \rho \end{pmatrix},$$

the three component factors corresponding to surface, body and surface of the filter respectively; ρ is the ratio of the reflected to the transmitted light for one surface only, and τ is the transmission factor for the body of the filter. On putting $N' = 0$ we get as the total transmission factor measured by a correct method

$$\frac{P'}{P} = \left\{ \frac{(1 + \rho)^2}{\tau} - \rho^2 \tau \right\}^{-1} = T \text{ say.}$$

If now this filter is followed by a second for which the matrix is m_1 , the fundamental equation is

$$(PN) = (P''N'') m_1 m,$$

and the combined transmission on the assumption that the second filter only differs from the first in transmitting τ_1 instead of τ is

$$\frac{P''}{P} = \left[\left\{ \frac{(1 + \rho)^2}{\tau} - \rho^2 \tau \right\} \left\{ \frac{(1 + \rho)^2}{\tau_1} - \rho^2 \tau_1 \right\} - \rho^2 \left\{ \frac{1 + \rho}{\tau} + (1 - \rho) \tau \right\} \right. \\ \left. \times \left\{ \frac{1 + \rho}{\tau_1} + (1 - \rho) \tau_1 \right\} \right]^{-1}$$

or

$$TT_1 \left[1 - \left(\frac{\rho}{1 + \rho} \right)^2 (1 + \tau T) (1 + \tau_1 T_1) \right]^{-1}.$$

The quantities measured are T and T_1 . We can assume a value for ρ with sufficient accuracy, and for τ substitute the approximate value $T(1 + \rho)^2$. The expression for the computed joint transmission is then

$$TT_1 \left[1 - \left(\frac{\rho}{1 + \rho} \right)^2 - \rho^2 (T^2 + T_1^2) - \rho^2 (1 + \rho)^2 T^2 T_1^2 \right]^{-1}.$$

The author's calculated transmission 0.07548 has been obtained on the assumption that no reflected light enters into the problem. If we apply the theoretical corrections for refractive index μ we have $4\mu\rho = (\mu - 1)^2$, and this gives the following calculated transmissions, when

$$\mu = 1.5, \quad \text{transmission} = 0.07563,$$

and when

$$\mu = 1.6, \quad \text{transmission} = 0.07574.$$

Either of these values changes the sign of the difference between the observed and calculated results. The refractive index of the specimens used in this test is likely to be nearer 1.5 than 1.6, and as the surfaces were not freshly polished at the time of the test the reflected light would be somewhat less than the value derived from the refractive index. A transmission value close to 0.07560 is as likely as any we might suggest, and the comparison of this figure with the observed value 0.07558 leaves nothing to be desired.

Dr W. D. WRIGHT. It would be interesting to know whether Mr Follett's experience with the cylindrical sector he describes would lead him to recommend it for general use in the laboratory. The calibration evidently depends on the position of the various optical parts in relation to this sector; thus, any transverse movement of the light beam or longitudinal change of focus would upset the calibration. While it is not difficult to ensure that such movement shall be absent in a complete instrument made in a factory, the same does not always follow in apparatus assembled in the laboratory.

AUTHOR's reply. I entirely agree with Mr Guild's view that the merits of a photoelectric spectrophotometer should be judged only from the results of comparisons with instruments of known reliability. This statement may seem inconsistent with the fact that only two results are given, but unfortunately we had no time before delivering the instrument to carry out all the tests we should have liked to make, and the results of the two tests given in conjunction with the test on the sector itself, as detailed in the paper, seemed so satisfactory that we felt justified in letting it go. We are hoping to put together another exactly similar instrument shortly; further tests will then be applied, and the results will be published.

I am grateful to Mr Smith for the details of the correction to be applied to the calculated values of the transmission of the two glasses together. Actually I had not overlooked the possible necessity of a correction, but a rough calculation satisfied me that the effect was negligible. Evidently my calculation was rougher than I thought, but I am relieved to find that the modification does not spoil the agreement between the calculated and observed values. Actually there is no experimental justification for the fifth figure in the results I gave—it would have been better to express the figure to four decimal places only; as it stands it may give an exaggerated impression of the sensitivity of the instrument. This does not affect the value of Mr Smith's remarks, of course; but the present seems a suitable opportunity of calling attention to the point.

I agree with Dr Wright that absolute rigidity of the mounting of the sector and optical system is necessary if accurate results are to be obtained with the cylindrical sector. It follows that the sector is hardly suitable as a general-purposes accessory for laboratory use; its proper use is in a permanent assembly.

NOTE ON THE PURITY REQUIRED FOR SURFACE-TENSION MEASUREMENTS

By T. C. SUTTON, M.Sc., F.INST.P., AND H. L. HARDEN, B.Sc.,
Research Department, Royal Arsenal, Woolwich.

Received January 25. Read April 20, 1934.

ABSTRACT. The extent to which impurities affect the measured value of the surface tension of a liquid depends on the method of measurement employed. This effect is applied to test whether the purity of a sample is adequate for the measurement of the surface tension of the pure liquid.

IN the course of measurements of the surface tension of some liquid explosives, the well-known differences between the values obtained for the surface tension by dynamic and by static methods of measurement and the effect of impurities on these values⁽¹⁾ have been applied as a means of checking whether the purity of a sample is adequate for measuring the surface tension of the pure liquid.

The table refers to measurements made during the purification of an organic liquid (nitroglycerine), analysis of which was both difficult and not sufficiently sensitive. The effect of residual impurities is conspicuously greater with the capillary methods than with the bubble-pressure method. Agreement between the three methods is an indication that (i) the purity is adequate and (ii) the value obtained is that of the pure material.

Surface tension (dyne/cm.)			Remarks
Bubble-pressure method	Capillary methods		
Sugden's ⁽²⁾	Ferguson and Kennedy's ⁽³⁾	Sutton's ⁽⁴⁾	
49.1	43	38	After preliminary drying and filtering
49.8	45	42	After further drying and filtering
50.3	50	51	After repeated drying and filtering. Value unaltered by further treatment

A sample of 2.0 cm³ was sufficient for test by these three methods. The test may be applied, however, to much smaller quantities of material by suitably selecting two capillary methods for the purpose.

This test of purity does not consume the sample.

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DISCUSSION

Dr A. FERGUSON. Obviously it is not necessary to employ the three methods to test the purity of the material under consideration—the three methods are approximately of the same order of sensitiveness, and any one of them is adequate. It is only necessary to purify the material under test until a constant value is obtained.

The figures given open up a number of important considerations, especially that of the variation of surface tension with time. This question has not received the consideration which it merits, and one of my students has recently made a study of the relation between surface tension, concentration, temperature and time. The solutions used were colloidal in character and a number of hitherto unsuspected relations have been brought to light.

Reply by Mr T. C. SUTTON. I could agree entirely with the remarks of Dr Ferguson were purification always a simple process and were its results always determinate.

In many cases, however, such as those with which we have been dealing at Woolwich, there may be no ready means of telling when a process of purification has yielded a pure sample and when, for example, a "constant-composition mixture" has been obtained. Such mixtures—for instance, certain mixtures of homologues—have frequently been found to be beyond the powers of analysis, and may easily be mistaken in practice for pure substances. Some further test was desired, and we were glad to find that the relevant purity of our sample could be checked by an expeditious means independent of the method of purification employed.

VELOCITY MODULATION IN TELEVISION

By E. E. WRIGHT, Baird Television, Ltd.

Communicated by Dr Lewis Simons, January 17, 1934. Read April 20, 1934.

ABSTRACT: The motion of a spot of light of constant intensity, necessary to produce the effect of a sinusoidal linear distribution of light-intensity on a television viewing screen, is determined and the effect of the finite size of the scanning spot is compared with the analogous effect in the more usual type of television system in which the scanning spot moves with constant speed and is modulated in intensity.

§ 1. INTRODUCTION

ACCORDING to the method of velocity modulation, a desired visual or photographic effect of light and shade-distribution is obtained by moving a spot of light of constant intensity along a scanning-line at a varying velocity.

If the size of the light-spot is small compared with the details to be reproduced, the motion required to produce a given shade-distribution is approximately obtained by making the velocity at any point inversely proportional to the required brightness at that point. If, however, the size of the light-spot is comparable with the size of the details, then a more refined analysis is required to determine the necessary motion.

§ 2. THEORY

If a rectangular light-spot of unit intensity and width $2W$ moves so that its median line is displaced through a distance x at a time t and if the velocity is always positive, then the motion necessary to give a shade-distribution $f(x)$ is defined by the equation

$$\int_{x-W}^{x+W} \frac{dt}{dx} dx = f(x) \quad \dots\dots(1).$$

In this preliminary analysis a simple periodic distribution defined by

$$f(x) = A + B \cdot \cos x$$

is considered. With this distribution equation (1) will be satisfied when

$$t = Ax/2W + \frac{1}{2}B \cdot \operatorname{cosec} W \cdot \sin x \quad \dots\dots(2),$$

and in a sense this solves the problem of determining the motion, but in order to draw conclusions it is necessary to obtain x explicitly in terms of t .

Putting $T = 2Wt/A$ and $C = (WB \cdot \operatorname{cosec} W)/A$, we reduce equation (2) to

$$T = x + C \cdot \sin x \quad \dots\dots(3).$$

If x is increased by 2π then T is also increased by 2π , and if the sign of x is reversed, so is the sign of T , hence if

$$x = T + \phi(T) \quad \dots\dots(4),$$

it follows that $\phi(T)$ is a periodic odd function, of period 2π , and is therefore adequately given by

$$\phi(T) = \sum_{n=1}^{\infty} A_n \sin nT \quad \dots\dots(5).$$

$$\text{Now, } \pi A_n = \int_0^{2\pi} x \cdot \sin nT \cdot dT - \int_0^{2\pi} T \cdot \sin nT \cdot dT = \frac{1}{n} \int_0^{2\pi} \cos nT \cdot dx \quad \dots\dots(6),$$

by integration by parts and use of equation (3).

The integral in equation (6) is easily reduced to a known form* and we have

$$\begin{aligned} \pi n A_n &= \int_0^{\pi} \cos(nx + nC \cdot \sin x) dx + (-1)^n \int_0^{\pi} \cos(nx - nC \cdot \sin x) dx \\ &= \pi J_n(-nC) + (-1)^n \pi J_n(nC) = 2(-1)^n \pi J_n(nC) \quad \dots\dots(7), \end{aligned}$$

where $J_n(nC)$ is a Bessel coefficient of order n . Hence the equation of the necessary motion is

$$x = T + \sum_{n=1}^{\infty} \frac{2(-1)^n}{n} J_n(nC) \cdot \sin nT \quad \dots\dots(8).$$

In practice the constant-velocity part of this motion is produced by a local oscillator generating saw-toothed wave-form at the receiver, and a signal to produce the periodic part only is transmitted.

§ 3. COMPARISON OF FINITE-APERTURE EFFECTS

In an ordinary television system, in which the scanning spot of width $2W$ moves with a constant velocity V and is modulated in brightness, it can be shown that†, owing to the finite size of the aperture, in order to produce a periodic distribution of shade $B \cdot \cos x$ it is necessary to transmit a signal of the form $WB \cdot \operatorname{cosec} W \cdot \cos Vt$.

The aperture effects in the two systems may therefore be compared as follows: when the width of the scanning spot approaches the wave-length of the shade-distribution or a multiple of this wave-length, then, in the case of an ordinary television system, the amplitude of the transmitted signal, which is a pure alternating current, increases rapidly, whereas in a velocity-modulation system the signal increases in complexity in the sense that its higher-frequency Fourier components become increasingly important constituents of the signal.

* T. M. MacRobert, *Spherical Harmonics*, p. 252 (Methuen 1927).

† *Bell System Technical Journal*, 6, 602 (1927).

DISCUSSION

Mr J. H. AWBERY. I find it of distinct interest to notice how frequently methods and results in pure mathematics are applicable in quite unrelated fields of physics. Thus the author's equation (3) is identical, except for the sign of the quantity C , with Kepler's equation* in astronomy, which connects the mean anomaly with the excentric anomaly of a planet. In that case, the reversion of the equation is the author's equation (8) with the factors $(-1)^n$ omitted, corresponding to the fact that $J_n(-nC) = (-1)^n J_n(nC)$.

The equation is particularly interesting, because it led Bessel to the discovery of his functions†, and also because it was the first transcendental equation satisfactorily solved by Lagrange, who gave the same solution, but with the Bessel functions† written out as series.

* R. S. Ball, *Spherical Astronomy*, p. 156 (London: 1908).

† L. Silberstein, *Synopsis of Applicable Mathematics*, p. 96 (London: 1922).

THE LONGITUDINAL THERMOELECTRIC EFFECT: (1) COPPER

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ABSTRACT. The e.m.f. produced by asymmetrical temperature-distributions in a copper wire is examined, and found to agree well with the formula

$$F = tG + a(G.G)^{\frac{1}{2}}G + b(G.G)G,$$

where F is the potential-gradient at the point where the temperature-gradient is G . The two constants a and b are calculated, and their dependence upon tension in the wire investigated. Their values are given by the formulae

$$a \cdot 10^{10} = -15.5 + 14.2W + 25.0 \exp(-W),$$

$$b \cdot 10^{12} = 47.8 - 20.5W - 50.0 \exp(-0.45W),$$

where W is the load in kilograms on the wire of diameter 0.885 mm.

§ 1. INTRODUCTION

ACCORDING to the statistical theory of thermoelectric phenomena expounded by Sommerfeld and Frank⁽¹⁾, a conductor in which no electric current flows, but in which a temperature-gradient is maintained, will show a potential-gradient which is proportional to the temperature-gradient. This simple linear relationship is usually accepted as accurately describing the experimental facts. It seems always to be assumed that, no matter what shape the temperature curve may take, if the two ends are at equal temperatures the total Thomson e.m.f. integrates to zero.

This assumption was expressed as the "law of Magnus"⁽²⁾, which stated that in a circuit composed entirely of one homogeneous metal no e.m.f. could exist, whatever temperature-distribution might be introduced. The fact that an e.m.f. was later discovered in a simple iron wire when asymmetrically heated⁽³⁾ was explained as due to lack of homogeneity of crystalline structure of the iron.

Benedick's results for copper⁽⁴⁾ have not been accepted as a contradiction to the law of Magnus. He used the constriction method to maintain the asymmetrical heating: a sharp point on the end of the heated piece of metal was pressed against the large piece of cold metal; at the point of contact is the very high and quite unmeasurable temperature-gradient. Secondary effects could so easily be introduced by the

constriction method that little weight has been attached to his results: see the work of Zernicke⁽⁵⁾ and Bernade⁽⁶⁾.

Experiments on the manifestly homogeneous metal mercury have so far failed to produce consistent results^{(4), (5)}; and the work of Seth, Anand and Anand⁽⁷⁾, purporting to show the existence of the e.m.f. in homogeneous copper wires without constrictions, is not quantitative enough to settle the question. These workers did not realize the necessity of an analysis of the temperature-distribution, and so missed the significance of their results altogether.

In the present work we have examined a copper wire again, but with a far more precise analysis of the temperatures. It now appears that the e.m.f. can be regarded as of like nature with the Thomson potential as defined by Sommerfeld and Frank, but slightly generalized.

The potential-gradient is shown to be a function of the temperature-gradient alone, but not a simply linear function. Quadratic and cubic terms are needed, which give finite e.m.f. on integration over an asymmetrical temperature-distribution between equal end temperatures. It may be best to retain the term *Thomson potential-gradient* for the linear factor, and so distinguish between it and the factors responsible for the e.m.f. which arises in asymmetrical states.

A quadratic term was at first thought to be inadmissible, since no e.m.f. is observed in perfectly symmetrical states; but finally we found it possible to introduce the term vectorially so that it gave zero e.m.f. for a symmetrical distribution, as required.

§ 2. APPARATUS AND TECHNIQUE

The apparatus for producing controllable asymmetrical temperature states was made to the design shown in figure 1. At one end is a water-cooling jacket, which abuts immediately upon the slate former of the central heating-coil. At the other

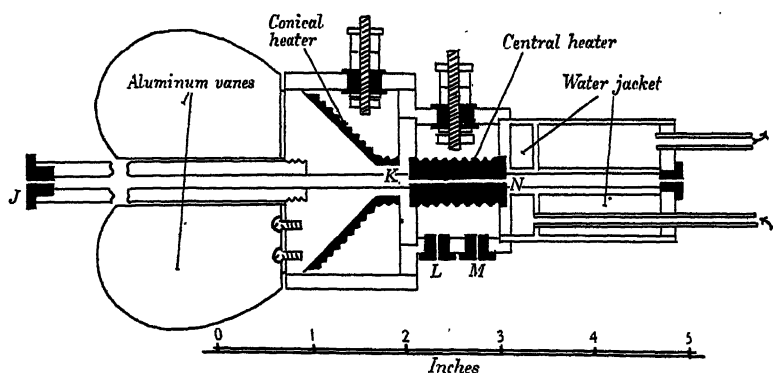


Figure 1. Section through apparatus for producing asymmetrical temperature-distribution. *J*, orifice for temperature probe; *K*, *N*, positions for comparison with figure 2; *L*, *M*, orifices for fixed thermocouple leads.

end of the central heater is a conical brass piece forming the core of another heater, which can be controlled independently of the central heater. To the back of the

cone are attached several aluminium radiators and, axially, a long brass rod down the centre of which the specimen wire is carried. Gradual cooling to room-temperature takes place down this narrow tube, and both ends of the specimen are thus maintained at about the same temperature. Since the specimen was a copper wire, copper leads were taken to the potential-measuring instrument.

Two copper-constantan thermocouples are attached permanently to the ends of the central heater to indicate the high temperatures. Another couple is used as a probe from the ends, for exploring the temperature state. A fine copper wire is first wrapped with thin paper, and a fine constantan wire placed in contact with this; the whole is then wrapped again in thin paper; and the ends of each wire project from the sleeve so far that the thermojunction can be made. Provided that temperatures are not taken too high, this kind of probe proves very satisfactory.

To obtain an accurate map of the temperature state, we first get an idea as to where the critical points are situated, the position in the water-cooled section where the temperature suddenly starts to increase, and the point near the maximum where the steepest gradient ends.

The error in temperature caused by the process of probing would be greatest in the steep gradient. For this reason, when the probe thermocouple was inserted through the water-cooled end, we used it only to find the critical point at which the temperature suddenly began to rise. All the other temperatures for which the probe was used were found by inserting it through the other end. Thus the probe did not disturb the steep gradient at all, and the position of the critical point was found to within about 0.2 mm. either way. The steep gradient was found by interpolation between the cold temperature point and the high temperature registered by the first fixed thermocouple in the heater. One source of error lies in the finite size of the fused contact between the couple and the wire, which is nearly 0.5 mm. long. The maximum probable error in our final results due to these various sources is estimated as about 4 per cent.

In finding the small gradient by the probe process we noticed that the thermocouple readings obtained while the probe was gradually inserted through the end differed by no more than 2 or 3 per cent from those obtained as the probe was gradually withdrawn. The enclosure acts as a shield or guard-ring, and the heat-flow is chiefly along the wire. Further, the heat-capacity per cm. of the enclosure is at least 500 times greater than that of either the specimen or the probe. We should thus expect that ideally slow probing would introduce negligible changes in the temperature of the enclosure and of the specimen wire when a steady state is obtained. In practice small changes in the e.m.f. were found to accompany the temperature-variations introduced by the probe, but these errors can be averaged out and are less significant than the errors made in estimating the steep gradient.

For the present work we decided not to attempt the use of a potentiometer; the most sensitive type available here being sufficient only for a minimum reading of $0.5 \mu\text{V}$. Instead we use a high-sensitivity galvanometer* of resistance 15Ω

* No current should be drawn if our results are to be described as e.m.f. measurements, according to Sommerfeld's remarks (1).

manufactured by the Cambridge Instrument Co., Ltd. This meter has a sensitivity of 2 cm. deflection at 1 metre for 1 μ V.

After the e.m.f. for any particular temperature state had reached its steady value, the e.m.f. was recorded between each reading of temperature made during the mapping. This mapping is accomplished by first finding the temperatures of the critical points, and then probing at intervals of 1 or $\frac{1}{2}$ cm. along the rest of the wire.

To eliminate as much as possible of the error thus introduced the temperature map was found by retracing the steps once or twice; the mean curve thus obtained was then used for correlation with the mean value of the e.m.f. found during the whole process.

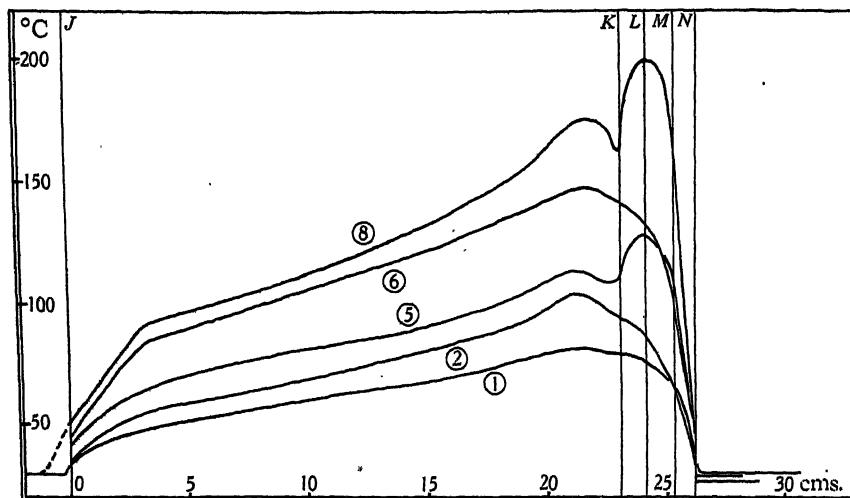


Figure 2. Typical temperature maps. The numbers correspond to those given in § 3. *K*, *L*, *M*, *N*, are positions corresponding to those in figure 1.

A further source of error is that some difficulty was experienced in keeping the heating-currents constant, owing to sudden fluctuations in the mains; but this error must be of less significance than those mentioned already, since continual watch was maintained on the heating-current and its controls.

The only way to increase the precision of our results would be to use smaller temperature-gradients. These could be measured more precisely and directly by means of fixed thermocouples at points near the ends of either gradient. But the smaller e.m.f.'s produced would necessitate a more sensitive galvanometer in order to permit of their estimation with the same degree of precision as the temperature-gradients. With the meter used in the present work higher precision in measuring temperatures would have been useless.

The heating-coils are wound non-inductively, but for the present work on copper this point is probably of no significance; work on iron will however be attempted shortly. Reversal of the heating current had no effect on the e.m.f., which is thus not disturbed by leakage from the heater on to the specimen.

The best temperature curves seem to be those, figure 2, for which the central heater carries the smaller current, for the others show an unfortunate hollow between the two heaters. While the present design gives the possibility of a very wide choice in types of curves, and is thus useful in preliminary work, higher accuracy could be obtained by using only one heater and relying upon shielding-tubes to produce the slow gradient on one side. This we are doing for further work already commenced.

The present apparatus is thus suitable to show that no matter how complicated the temperature state may be we can still correlate the e.m.f. with the temperature-gradient, and thus demonstrate that it is a true Thomson potential in a slightly generalized sense.

No special precautions were taken with regard to the chemical purity of the specimen; the investigation of the effect of impurity and previous mechanical and thermal treatment would make an important field for further study.

§ 3. RESULTS

The results of our measurements are analyzed with the help of the following simple theory. Let the vector electric potential-gradient be \mathbf{F} , and the vector temperature-gradient be \mathbf{G} , and assume that

$$\mathbf{F} = t\mathbf{G} + a(\mathbf{G} \cdot \mathbf{G})^{\frac{1}{2}} \mathbf{G} + b(\mathbf{G} \cdot \mathbf{G}) \mathbf{G} \quad \dots\dots(1),$$

where t is the Thomson potential-gradient of Sommerfeld and Frank, and a and b are new constants to be derived from our results.

It may be pointed out here that we must use the vector notation in order to include the second term in the expansion (1). A quadratic term in scalar form would give an experimentally incorrect expression, resulting in an e.m.f. under a purely symmetrical temperature-distribution.

To find the total e.m.f. E developed in a wire along which \mathbf{G} is directed, we have to integrate:

$$\begin{aligned} dE &= \mathbf{F} \cdot d\mathbf{x} \\ &= t\mathbf{G} \cdot d\mathbf{x} + a(\mathbf{G} \cdot \mathbf{G})^{\frac{1}{2}} \mathbf{G} \cdot d\mathbf{x} + b(\mathbf{G} \cdot \mathbf{G}) \mathbf{G} \cdot d\mathbf{x}, \end{aligned}$$

and since $G = dT/dx$ in magnitude, this may be written

$$E = t(T_1 - T_2) + \int a(\mathbf{G} \cdot \mathbf{G})^{\frac{1}{2}} dT + \int b(\mathbf{G} \cdot \mathbf{G}) dT \quad \dots\dots(2),$$

where T_1 and T_2 are the end temperatures of the wire.

If the two ends of the wire are at the same temperature, then of course equation (2) shows that the normal Thomson potential-difference vanishes identically. Only if the temperature-distribution is symmetrical, however, will the a and b terms give also a zero result. On division of the curve into suitable sections these two terms can in any particular case be evaluated without difficulty. Thus

$$E = a\Sigma (G dT) + b\Sigma (G^2 dT) \quad \dots\dots(3),$$

where in the first term the positive magnitude of G must be used without regard to the sign of the gradient.

Altogether eight different temperature states were examined in the first test, of which five are shown in figure 2. The wire was under tension due to application of a weight of 1 kgm. at each end. In each case it was noticed that the positive current flowed from parts with great G to parts with small G , in the wire: on open circuit there should therefore be an accumulation of electrons in the specimen at the base of the steeper temperature-gradient.

By grouping the curves into pairs thus: nos. 1 and 5, 2 and 6, 3 and 7, 4 and 8, we calculate the average of the four values thus obtained for the constants a and b . The result was:

$$a = 7.90 \cdot 10^{-10} \text{ volt-cm./}({}^{\circ}\text{C.})^2,$$

$$b = -4.65 \cdot 10^{-12} \text{ volt-cm}^2/({}^{\circ}\text{C.})^3.$$

These values are used to calculate the theoretical e.m.f. in table 1. Here I_1 is the current in amperes in the central heater, I_2 the current in the conical heater; E is the observed e.m.f. in microvolts averaged over all the values taken during the mapping of the corresponding temperature-distribution; MD is the mean deviation of the individual values of e.m.f. during this process; A is the term $\Sigma (GdT)$ and B the term $\Sigma (G^2dT)$ in equation (3) above. The theoretical value of E is thus found from $E = aA + bB$.

Table 1

Curve	I_1	I_2	E	MD (per cent)	$A \cdot 10^{-2}$	$B \cdot 10^{-4}$	$aA + bB$
1	2.0	4.5	0.83	4.4	13.86	5.619	0.83
2	1.4	6.0	1.19	3.1	19.20	7.967	1.15
3	2.2	5.0	1.19	2.4	20.87	8.752	1.23
4	2.4	5.0	1.68	1.1	28.35	13.30	1.62
5	3.0	6.0	2.18	0.9	42.46	25.92	2.15
6	2.3	7.0	2.46	2.0	53.25	39.96	2.35
7	1.5	7.6	2.46	1.3	55.01	39.15	2.53
8	3.0	8.0	2.89	1.7	173.0	240.0	2.76

The values of MD are unfortunately somewhat large in several cases, and this indicates that the probe method of finding the temperature-distribution had a disturbing effect not altogether negligible.

In order to find, if possible, the dependence of the two constants on the tension, similar work was carried out while the wire was kept under a series of different tensions. The results are given in the graph of figure 3.

In general we can remark that apparently both a and b have non-zero values as the tension approaches zero. But our values for the smallest tension measured are not very reliable, because the weight used ($\frac{1}{2}$ kgm.) was not enough to straighten out the small bends in the wire; and these must introduce local irregularities in the strain of the material, only eliminated when the general tension is large enough to straighten out the wire.

As the tension increases to several thousand kgm./cm² the curve approaches linearity, both functions increasing with tension much more rapidly than for small tensions.

In figure 3 the full curves are plotted from the formulae

$$a \cdot 10^{10} = -15.5 + 14.2W + 25.0 \exp(-W),$$

$$b \cdot 10^{12} = 47.8 - 20.5W - 50.0 \exp(-0.45W),$$

where W is expressed as kilograms load on the wire. These formulae appear to give about the best fit, but little significance attaches to empirical formulae of the sort unless fortuitously. Thus in this case we have fitted formulae of the forms $a = a_0 + a'(1 + W^2/a''^2)^{\frac{1}{2}}$ and also $a_0W \exp(a'W^n)$ with nearly equal accuracy, but the latter formula makes the curve pass through the origin and ignores our results for the $\frac{1}{2}$ -kgm. load. A simple power series in W might also be found, but we chose the form used above as more directly representing the visible characteristics of the curves.

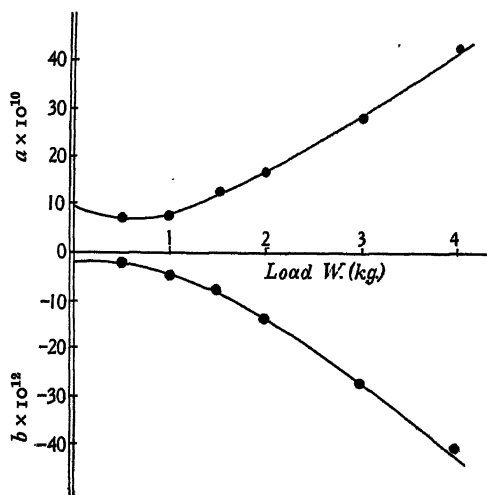


Figure 3. The two new thermoelectric constants as functions of tension. Small circles indicate values calculated directly from observations, and the full curves are plotted from empirical formulae. The values at $W = 1$ are most certain.

We suggest, on the basis of these results, that it would be better to determine more accurately the behaviour of the two constants under small tensions; probably by the use of thin rods suspended vertically, instead of wires. Since, however, the constants must obviously depend greatly upon previous treatment of the substance this was not possible with our specimen, which was a wire of mean diameter 0.885 mm.

§ 4. DISCUSSION OF RESULTS

We indicate first how a formula like (1) can be derived theoretically. In Fermi statistics⁽⁸⁾, the thermionic current across the face of a crystal is a function of the form

$$i = A \cdot T^2 \cdot e^{-E/T},$$

where A and E are constants, A depending on the number of electrons per cm^3 ,

and E upon the surface work function. If two crystals are in close contact in our wire specimen, the current flowing across the interface will be the differential

$$di = 2ATS \cdot dT + AT^2 \cdot dS,$$

where the value dS signifies the expansion as a series in dT of the differential of the exponential term. If E/T is large the result is found to be

$$di = - ASE \cdot dt + \frac{1}{2} ASE^2 \cdot dT^2/T^2 - \frac{1}{6} ASE^3 \cdot dT^3/T^3 \dots$$

and here dT is the temperature difference between the adjacent faces. Ordinarily we neglect the terms in dT^2 and dT^3 in taking differential coefficients, but in this case we see that this may introduce a serious error when dT is not really zero and E/T is large. Here dT will be proportional to G , the temperature-gradient in the wire, and so we find a form like that of equation (1).

We have pursued this idea in great detail but found finally that quantitatively the results are many orders too small to account for our observations. This probably means that the physical ideas at the basis of the work are erroneous; we include the foregoing remarks merely to point out the necessity for greater care in differentiating functions like the Fermi distribution function. The correction terms in G^2 and G^3 for the Thomson potential-gradient may be obtainable from a revision of Sommerfeld's calculations from this point of view.

The present work has been reported in some detail to prepare for a more concise account of future results.

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THE LINKAGE OF CO₂ AND CO

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ABSTRACT. New calculations of Adel and Dennison make it possible to show that the ground level of CO₂ arises adiabatically from C ($p^4\ ^3P$) + O (3P) + O (3P), or in other words that the linkage of the carbon atom to either of the oxygen atoms is exactly the same and is due to a pronounced $p^2=p^4$ bond (O=C=O). Excitation in the ground level of the CO molecule of those two electrons which in the adiabatic dissociation become the s^2 group of carbon in such a way that in the dissociation they become two additional p electrons, brings about the carbonyl term of CO. Adiabatic dissociation of CO₂ into CO and O leads to the carbonyl term (=C=O) and an unexcited O. The linkage in CO has to be considered as a double link. The numerical agreement is very good.

IN a recent paper Adel and Dennison⁽¹⁾ have calculated the constants of the CO₂ molecule using the data of the infra-red spectrum. This enables us to determine the energy of adiabatic dissociation of carbon dioxide in a way which was not previously possible. In a recent note⁽²⁾ on the dissociation of PbO₂ the corresponding figures for CO₂ were not given, since at the time of writing they could not be compared with other values found by an independent method. It was shown that the combination of a Pb atom with two O atoms arises neither from the ground level of Pb ($s^2p^3\ ^3P$) nor from any of the levels of the configuration (sp^3), but from the anomalous 3P state with four equivalent p electrons, and it was mentioned that the linkage in CO₂ is probably of the same type.

The heat of formation of CO₂ from CO and O₂ is 67.62 k.-cal./mol.⁽³⁾ the best value obtainable for the heat of dissociation of O₂ is 117.4 k.-cal./mol. Hence

$$(\text{CO}) + \frac{1}{2} (\text{O}_2) = (\text{CO}_2) + 67.6 \text{ k.-cal./mol.}$$

$$(\text{O}) - \frac{1}{2} (\text{O}_2) = 58.7 \text{ k.-cal./mol.}$$

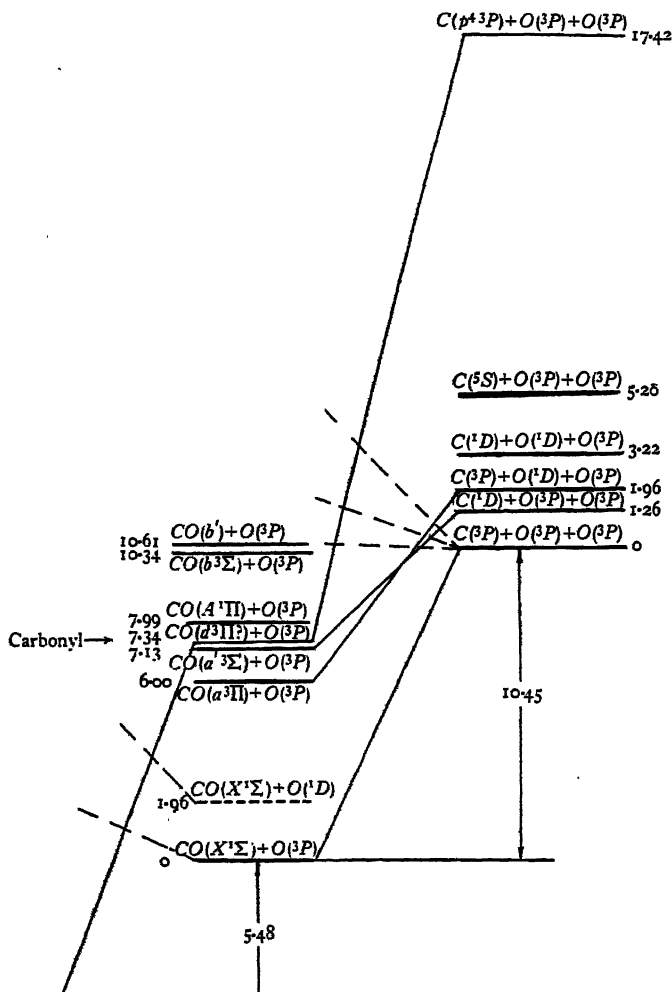
$$(\text{CO}) + \text{O} = (\text{CO}_2) + 126.3 \text{ k.-cal./mol.}$$

i.e. the ground level of the CO₂ molecule lies 126.3 k.-cal./mol. or 5.48 electron-volts below the ground level of the CO molecule and a separated O atom.

Carbon monoxide in its ground level dissociates into unexcited atoms. The extrapolation of the vibrational levels of the $^1\Sigma$ state gives a value for the dissociation energy which is clearly too high in the light of thermochemical data. Kaplan⁽⁴⁾ has suggested the possibility of obtaining the dissociation energy from the levels $b\ ^3\Sigma$ at 10.34 and $b'\$ at 10.61 V. These levels are sometimes considered to be not two distinct electronic levels at all, but consecutive vibrational levels of

the same state $b^3\Sigma$. This in our opinion is highly improbable, as b' does not combine with the ground state whereas $b^3\Sigma$ does, both in emission and in absorption. We can, therefore, say that the second vibrational level of $b^3\Sigma$, which might also lie at about 10.6 V., is already quenched by predissociation. The repulsive state to which the predissociation is due will originate at about 10.45 V., because it will be of a very flat character since it is clearly the lowest of the repulsive states. A still lower repulsive state, if it were capable of existence, would have quenched the first level at 10.34 V.

The value of 10.45 V. obtained in this way is also in good agreement with thermochemical data, if account is taken of the fact that these are subject to a certain error owing to the fact that the heat of sublimation of carbon is not well known for low temperatures. On the other hand our computation allows us to calculate this heat of sublimation spectroscopically. Denoting the heat of sublimation of carbon (β -graphite) by x , we have at 25° C.



$$[C]_{\beta\text{-graphite}} + \frac{1}{2} (O_2) = (CO) + 26.65 \text{ k.-cal./mol.}$$

$$(C) - [C]_{\beta\text{-graphite}} = x$$

$$(O) - \frac{1}{2} (O_2) = 58.70 \text{ k.-cal./mol.}$$

$$(C) + (O) = (CO) + (85.35 + x) \text{ k.-cal./mol.}$$

Since

$$(C) + (O) = (CO) + 241.05 \text{ k.-cal./mol. (= } 10.45 \text{ V.)}$$

for the heat of sublimation of carbon (β -graphite) at 25° C. we obtain

$$x = 155.7 \text{ k.-cal./mol.}$$

We can now return to the question of the adiabatic dissociation of CO₂. The carbon term $p^4 \text{ } ^3P$ is not measured, but can well be computed from the corresponding terms of the ionized atom in the usual manner*. Thus

$$C(2s \text{ } 2p^3 \text{ } ^5S) - C(2s^2 \text{ } 2p^2 \text{ } ^3P) = 5.20 \text{ V.},$$

$$C(2p^4 \text{ } ^3P) - C(2s \text{ } 2p^3 \text{ } ^5S) = 12.22 \text{ V.}$$

The total energy of dissociation of CO₂ into C($p^4 \text{ } ^3P$) + O(3P) + O(3P) is therefore $5.48 + 10.45 + 5.20 + 12.22 = 33.35 \text{ V.}$

Adel and Dennison⁽¹⁾ have obtained theoretical expressions for the energies etc., and calculated the occurring constants in accordance with the infra-red spectrum. Thus for the energy of dissociation of CO₂ into CO and O they get the value

$$103750 \text{ cm}^{-1} \text{ or } 12.80 \text{ V.}$$

It can be deduced from the data given in that paper that the energy of dissociation of the CO molecule in that excited state in which it is left when CO₂ is stripped of its first O atom or, so to speak, is in the state in which it is able to receive a second O atom, is

$$166350 \text{ cm}^{-1} \text{ or } 20.53 \text{ V.}$$

Hence the total energy of dissociation of CO₂ obtained from the infra-red spectrum is

$$270100 \text{ cm}^{-1} \text{ or } 33.33 \text{ V.},$$

and is in surprisingly good agreement with the value of 33.35 V., calculated above. The difference of 7.73 V. between the energies necessary for the dissociation of the first and second O atoms is due to the repulsive force between the O atoms. Now it can definitely be said that tetravalent carbon, in CO₂ at least, possesses four p electrons, the two s electrons of divalent carbon having been promoted to the p shell.

Since the ground level of CO₂ is a $^1\Sigma$ state and the O atoms are linked in their 3P states, removal of the first O atom leaves CO in a triplet state; most probably in a $^3\Pi$ state. This is certainly not the $^3\Pi$ state at 5.98 V., which was taken into

* In current literature the state $sp^3 \text{ } ^5S$ of C is sometimes supposed to be about 1.6 V. above the ground level. This value was assumed by Heitler and Herzberg (1929) in order to explain the intersection of potential curves of CN. The spectrum of C⁺, however, shows that the proper value is 5.20 V. (See also J. H. Van Vleck, who gives 5 to 8 V.⁽¹⁶⁾.) In this particular case owing to the greater number of p electrons the computation from the spectrum of the ion will yield even a better value than in other cases where it has been shown to give fairly exact results⁽⁵⁾.

consideration by Herzberg^{(6)*} and which dissociates into atoms of lower energy of excitation. The triplet state, we expect, must lie 12.80 V. above the CO₂ ground state, i.e. 7.32 V. above the ground-most state of CO, having an energy of dissociation of 20.53 V. We suppose that the state termed $d^3\Pi$ is the one in question†.

This triplet term which we have now obtained, whether it is identical with the $d^3\Pi$ state or not, is formed by tetravalent carbon with four equivalent p electrons and accordingly has two free p valencies. It is therefore the state from which compounds of the type $\text{R} \diagup \text{C}=\text{O}$ arise. CO in this state is the so-called carbonyl ($=\text{C}=\text{O}$). Only in the case where R is H is there no difficulty in using a carbonyl arising from C (sp^3). To our mind the above calculation definitely establishes that, at least in the state in question, the bond of radicles to the carbonyl is a true $p-p$ bond and that the possibility of a q bond suggested by Hund⁽⁷⁾ does not occur here; probably because the levels of CO arising from C (sp^3) and C (p^4) respectively are not sufficiently close, and do not approach each other either when radicles or a second O atom are brought near.

The fact that the *adiabatic* dissociation of the carbonyl leads us to a carbon atom in the $p^4\ ^3P$ state does not of course imply the assumption that the *chemical* dissociation proceeds in this manner. In speaking of an adiabatic dissociation we necessarily mean the continuation of the curve which would be the only one capable of existence if no perturbation occurred. This does not mean that by a non-radiating transition the molecule could not change to an intersecting curve, especially in cases where the multiplicities of the states concerned are equal; this change, therefore, not only is most probable but even might proceed along a slightly varied connexion, thus avoiding the point of intersection. In the example discussed in this paper there are clearly enough intersections of the adiabatic potential curve of the carbonyl state with other potential curves of the same multiplicity, even with such as go to the ground levels of the atoms, and the *chemical* dissociation therefore may easily end at C ($s^2 p^2\ ^3P$) + O ($p^4\ ^3P$).

The CO molecule is sometimes said to be triply linked and written as $\text{C}\equiv\text{O}$. This assumption, as far as band spectroscopy is concerned, is based on a theory developed by Herzberg and Mulliken. The two groups of electrons determining the bond in the ground state of CO are $\pi^4 (2p) \sigma^2 (2p)$, which doubtless are bonding in all the existing theories. The difference between the theories in this particular case amounts only to a different definition of valency. Herzberg and Mulliken count these six electrons as three pairs and in this way define a trivalency of the CO bond, no matter from which atom the single electrons originate. Hund⁽⁷⁾, on the other hand, counts only those pairs in which electrons from different atoms join, and in a recent paper⁽⁸⁾ along with considerations about the part played by disturbing electrons the authors have upheld the same point of view. This means

* The states to which Herzberg mainly attributes the CO₂ linkage are CO ($^1\Sigma$) and O (1D), to which we shall refer below.

† We are indebted to Dr R. K. Asundi for informing us that on the long-wave side of the $d^3\Pi$ level now recorded at 7.9 V. he has found several new heads belonging to this level, and that this fact is likely to bring ν_0 down to our value. This level is obtained under special conditions only in the presence of a rare gas, which may be due to the excitation of two electrons.

that, since two of the six p electrons in CO come from C and four from O, we have only two bonding pairs, and accordingly divalency obtains.

The difference between these two views is really only a difference in definition, and so it is impossible to prove by mathematical reasoning that either of them is incorrect. We can only ask which definition agrees better with the usual conception of valency. The definition which is wanted by chemistry is actually a definition of bonds *between the atoms*. The definition given by Mulliken and Herzberg, although it frequently leads to the same result as the other, certainly counts the number of bonds between the six p electrons without consideration as to whether these electrons go to the same atom or not in the dissociation. This, however, is not the question with which we are concerned. We wish to obtain information regarding the forces by which the nuclei are kept together. For our purpose the forces between the four p electrons of O are immaterial, and when we only consider the interaction between the C atom on one side and the O atom on the other side we come to divalency. According to the definition of Mulliken and Herzberg the same kind of trivalency would always prevail whenever six p electrons meet, not only in N_2 and CO, but also in BF and even in a BeNe; but it would be a trivalency which keeps only the six electrons of the p shell together, whereas the number of bonds between the nuclei of the partners are 3, 2, 1 and 0 respectively. Therefore only that definition which identifies the number of links with the number of pairs of electrons from different partners meets the requirements of chemistry.

It has sometimes been suggested⁽⁹⁾ that the value 10.45 V. of the dissociation energy of CO points towards a triple linkage on the basis of an average value of approximately 3 V. per link. It is intended to deal with this question at greater length in connexion with general problems of valency; so attention may be confined at this stage to mentioning only that certain regularities can also be produced without Herzberg and Mulliken's method of counting the valencies. In the oxides of the lighter elements 5 V. per link appears to be a truer value than 3 V. if in the case of perturbing electrons we deduct an appropriate amount for perturbation. Thus the dissociation energy is 4.7 V. for OH, 5.75 V. for BeO which is singly linked⁽⁸⁾, and 10.45 V. for CO which is doubly linked. Again, in NO the dissociation energy is 6.7 V. so long as the linkage is perturbed but increases to 10.67 V. as soon as the perturbing electron is excited⁽⁸⁾. We cannot therefore expect N_2 to fall into line with the oxides and to show a dissociation energy of 15 V. for the triple bond because of the lower electronic affinity of N. A theory which implies a constant value for the stability of the bond, irrespective of the atoms concerned, cannot be physically sound, since stability must depend on the charges of the nuclei, or (what is the same thing) on ionization potential and electronic affinity. Already rough calculation indicates that we cannot compare a double and a triple link in this manner. If only for the purpose of rough calculation and without any great assumption of accuracy we set the energy of the σ^2 group equal to half the energy of the π^4 group, we can say that the splitting of the σ^2 group and the π^4 group needs six-ninths or eight-ninths of the total energy according to whether we split the π^4 group into 1 + 3 or 2 + 2 electrons, since in the first case three and in the second case five of the six mutual interactions in π^4 undergo fission. That means

that even when the conditions are not altered by any change in the nuclear charges the transition from a double to a triple link would increase the energy of dissociation not by 50 per cent but only by about 33 per cent.

Herzberg and Mulliken's enumeration would certainly be correct, if the above compounds dissociated adiabatically with always the same distribution of the p electrons, i.e. N_2 into $N + N$, CO into the ions $C^- + O^+$, and BF into $B^{--} + F^{++}$; and even a combination of Be^{---} and Ne^{+++} would not only be possible, but also give rise to a triply covalent $BeNe$. In the case of the CO molecule it is a well-established fact that CO in its ground state dissociates into unexcited atoms, and in the ordinary adiabatic way and without intersection of an ionic curve^{(10)*}. Also in chemical literature a triple link is sometimes ascribed to the molecule of carbon monoxide⁽¹¹⁾. Three arguments are given, viz. the proportionately high frequency in the Raman effect, the difference of the dipole moments of carbon monoxide and the carbonyl radicle, and the preservation of the octet rule. The frequency of the Raman line depends on the energy of dissociation and the anharmonic constant of the vibration. If we neglected the possible difference of anharmonicity, a high Raman frequency would denote only a high energy of dissociation, and we have already pointed out above that the dissociation energy of 10.45 V. is by no means an exceptionally high value among those of the oxides of the light elements, and that equal energies of dissociation do not mean an equal number of bonds. Since, however, the Raman frequency is a function also of the anharmonicity, its value gives still less evidence of a triple link. Nor can the dipole moment be taken as a measure of the number of bonds. In view of the electronic configuration of CO in its $^1\Sigma$ state it is only surprising that a dipole moment is present at all in the molecule, indicating a slight polarization of the molecule in spite of its covalent linkage. We have shown above that the carbonyl radicle arises from the carbon monoxide by excitation of two electrons, or perhaps of one in exceptional cases. The symmetrical electronic configuration of carbon monoxide is thus perturbed, and it would be most amazing if a considerable dipole moment did not arise from this perturbation, especially in those cases in which the two former s electrons of C then forming an s^2 shell of spherical symmetry are now literally bound to the side opposite to the O atom. These two tests failing, there is no physical reason whatever to assume a particular exception for the linkage of the CO molecule for the sole purpose of the preservation of an orthodox octet rule. It may be added that chemical evidence also does not appear to favour the preservation of the octet rule⁽¹²⁾.

Whether the CO linkage is considered to be double or triple, it is clear from this discussion that it is brought about by the two p electrons of unexcited carbon. The importance of the conclusions drawn here from Adel and Dennison's calculations

* Pauling on his assumption of 3 V. per linkage has attempted to show that CO in its ground state is actually bound as $C^- O^+$. His proof is not conclusive since wave mechanics yields no possibility of exchanging part of the energy curve of one molecular state for that of another. If two potential curves intersect, perturbations occur only at those vibrational levels at which the intersection takes place and in their vicinity, i.e. at those levels for which the energies of the states are exactly or nearly equal.

lies in the proof that the C atom in CO₂ possesses definitely four equivalent *p* electrons. Adiabatically stripping it of an O atom leads us to an excited CO molecule, to be called the carbonyl state of CO, in which C and O are linked by two *p* electrons of carbon whilst two more *p* electrons of the C atom are open to other linkages, which then become true *p*—*p* bonds.

In former discussions it was sometimes assumed⁽¹³⁾ that the CO state responsible for either CO₂ or for the carbonyl or for both of them arises from C (*sp*³), which we see now is only possible in compounds in which an H atom is linked to the C atom. Another assumption is that CO₂ arises by combination of CO in its ground state with O in its ¹D state, and that the carbonyl radicle is a CO molecule in one of the ordinary excited triplet states of which a ³Π is the lowest*^{(6), (14), (15)}. This is not only inconsistent with the new results but also open to other objections. CO (¹Σ) + O (¹D) would probably give rise to repulsive states only and would not be compatible with the equivalency of the two O atoms which is established by both optical and chemical evidence. Furthermore, the ordinary excited triplet states of CO, which would according to Mecke be the carbonyl states, arise from the ground state when one of the bonding groups undergoes fission, which in any case means the loss of a link. Even if we call the CO linkage a triple link, the newly arising two valencies would have to be located either on the side of O only or one at O and one at C. If, however, we term the CO linkage a divalency, which we have explained to be more sound, a carbonyl with a single link between carbon and oxygen, and the free valencies again located one at carbon and one at oxygen thus (—C—O—), would remain, and this is not the chemical carbonyl group. It is quite true that the electrons of the same group in the molecule are equivalent and that on account of their exchange a particular electron cannot be ascribed to a particular nucleus; but apart from other reasons already mentioned, the use of structural formulae implies that at any moment in each term a distinct number of electrons belong to a certain atom, especially as far as electrons corresponding to free valencies are concerned.

Mecke has attempted to explain the difference between the thermochemical energies of dissociation of CO₂ and CO which seems contradictory to the equivalence of the two oxygen atoms in CO₂. On the assumption that the products of dissociation of CO₂ into CO and O are normal CO and an excited O atom, he has found a value of about 5 or 15 k.-cal./mol. for the repulsive energy of the O atoms according to the excited term of O he has taken into account. This figure is in complete disagreement with the 7.73 V., equalling about 178.3 k.-cal./mol., which has been calculated by Adel and Dennison⁽¹⁾. The above discussion throws light on the question why the thermochemical energies of dissociation seem to be different. It is only with the help of the value of 7.73 V. for the energy of repulsion, without which the carbonyl state at 7.34 V. would lie exactly half way between CO (¹Σ) and C (*p*⁴ ³P) + O (³P) + O (³P), and on the consideration that the actual energies of the links to either O atom are strictly equal, that we arrive at a complete explanation of the facts observed.

* This state seems to dissociate into C (*s*^{2*p*² ³P) and O (*p*⁴ ¹D) since the extrapolated energy of dissociation indicates an atom excited by about 2 V. above the level of 10.45 V.}

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THE SPECTRUM OF TREBLY-IONIZED BROMINE, Br IV

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ABSTRACT. Vacuum spark and discharge-tube spectra of bromine have been investigated over a wide range. Many of the triplets and singlets involving the terms due to $4p$, $5s$, $4d$, sp^3 and $5p$ configurations have been identified. From the present work the classifications made by S. C. Deb appear to be incorrect. The deepest term $4p^3P_0$, which equals 404892 cm^{-1} , yields an ionization potential of about 50 volts for the trebly-ionized atom of bromine.

§ 1. INTRODUCTION

OUR knowledge of the spectrum of Br IV consists chiefly of the list of wave-lengths of lines attributed to Br IV by L. and E. Bloch⁽¹⁾ from experiments on the electrodeless discharge through bromine vapour, in the comparatively short region $\lambda 3261$ to $\lambda 2302$. The only attempt at the analysis of this spectrum has been that of S. C. Deb⁽²⁾ who arranged some of the lines into multiplets arising from the transition $5p \rightarrow 5s$ of the series electron. From the present investigation, however, the classification suggested by Deb appears to be erroneous.

In continuation of the work on the spectra of Br V, VI and VII⁽³⁾, a detailed investigation of the spectrum of Br IV has been undertaken. It is the purpose of the present paper to describe the results of the analysis of the lines due to the trebly-ionized atom of bromine. The experimental work which forms the basis of the present paper has been fully described in the previous paper on Br V, VI and VII. It may, however, be stated that in the quartz region many new lines have been recorded in addition to the list published by Bloch. By a careful study of the plates in the extreme ultraviolet region, taken under different degrees of excitation and covering the range $\lambda 430$ to $\lambda 1500$, the lines of Br IV have been selected.

§ 2. STRUCTURE OF THE SPECTRUM

The spectrum of Br IV is analogous to the iso-electronic spectra of Ge I, As II and Se III, the essential features of which are almost completely known⁽⁴⁾. This has considerably facilitated the analysis of the spectrum of Br IV. The theoretical term scheme of Br IV is given in table 1.

Table 1. Predicted terms of Br IV

3 ₁ 3 ₂ 3 ₃	4 ₁ 4 ₂ 4 ₃ 4 ₄	5 ₁ 5 ₂ 5 ₃	Term prefix	Terms
2 6 10	2 2	4 <i>p</i>	³ P ¹ D ¹ S
2 6 10	2 1 . .	1 . .	5 <i>s</i>	³ P ¹ P
2 6 10	2 1 1	4 <i>d</i>	³ F ³ D ³ P ¹ F ¹ D ¹ P
2 6 10	2 1 . 1	. . .	4 <i>f</i>	³ G ³ F ³ D ¹ G ¹ F ¹ D
2 6 10	2 1 . .	. 1 .	5 <i>p</i>	³ D ³ P ³ S ¹ D ¹ P ¹ S
2 6 10	1 3	5 <i>p</i> ³	⁵ S ³ D ³ P ³ S ¹ D ¹ P

The first evidence of the regularities in the spectrum of Br IV has been the discovery of the recurrence of the characteristic interval 2990 cm⁻¹ among several lines in the region about λ 570, which have been definitely ascribed to the trebly-ionized atom after a careful scrutiny of the plates. Some of the strongest lines in the spectrum are to be sought in the transition 5*s* → 4*p* of the series electron. By the application of the irregular doublet law to the lines due to the combination between the deep terms, it is expected that the chief triplet group 4*p*³P–5*s*³P lies in the region λ 550. In table 2 the position of the line 4*p*³P₂–5*s*³P₂ in the analogous spectra of Ge I, As II, Se III is shown, and the corresponding line identified in Br IV is included also.

Table 2.

Spectrum	4 <i>p</i> ³ P ₂ –5 <i>s</i> ³ P ₂	$\nu' = \nu - 2468(Z-A)^2$	$\delta\nu'$
Ge I	37708	35240	
As II	78967	69095	33855
Se III	126454	104242	35147
Br IV	180350	140862	36620

It is found that some of the above-mentioned pairs occur just in this region. A further comparison of these spectra made by the application of the regular doublet law to the intervals of the 4*p*³P₁–4*p*³P₂ in the sequence Ge I to Br IV has clearly indicated that the difference 2990 cm⁻¹ must be identified as the interval 4*p*³P₁–4*p*³P₂. The screening-constant for Br IV on this assumption is shown in table 3.

Table 3. Regular doublet law

Element	4 <i>p</i> ³ P ₁ –4 <i>p</i> ³ P ₂	$\sqrt{(\delta\nu/0.0455)}$	<i>s</i>	δs
Ge I	853	11.69	20.31	
As II	1477	13.42	19.58	0.73
Se III	2196	14.82	19.18	0.40
Br IV	2990	16.01	18.99	0.19

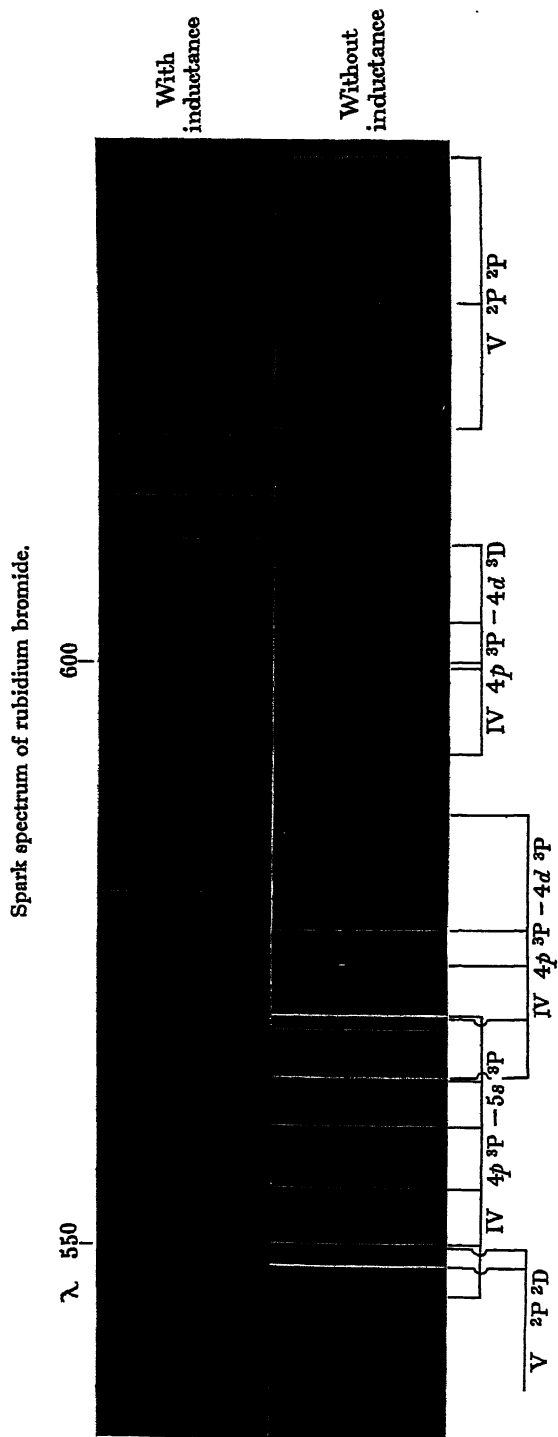


Table 4 gives the combinations identified in the present work. The starting-point for the classification is the identification of the ground multiplet $4p^3P-5s^3P$. The irregular doublet sequence, the progression of the screening-constant, and the uniform behaviour of the lines forming the multiplet (shown in plate 1) constitute

Table 4. Combinations in Br IV

	$4p^3P_0$ 404890 3247	$4p^3P_1$ 401643 2990	$4p^3P_2$ 398653	$4p^1D_2$ 386775
$5s^3P_0$ 224271 1281	177372 (9)			—
3P_1 222990 4688	181900 (9)	178653 (9)	175663 (6)	
3P_2 218302	—	183341 (5)	180350 (8)	
$5s^1P_1$ 215856		185787 (2)	—	
				170918 (9)
$4d^3D_1$ 235980 1115	168910 (9)	165659 (5)	—	150787 (2)
3D_2 234865 2856		166778 (8)	163786 (2)	151912 (1)
3D_3 232009			166644 (8)	154762 (1)
$4d^3P_0$ 225937 1625		175706 (10)		
3P_1 224312 — 3892	(180578)	177331 (8)	174340 (8)	—
3P_2 228204		173440 (10)	170447 (10)	—
sp^3D_1 250993 8053	153898 (6)	150648 (10)	147658 (5)	—
3D_2 242940 10608		158701 (10)	155710 (10)	—
3D_3 232332			166318 (10)	—
sp^3P_0 236555 — 348		165088 (5)		
3P_1 236903 — 419	(167987)	164740 (6)	161748 (5)	—
3P_2 237322		164322 (8)	161328 (7)	—
A 265711	139179 (10)	135933 (9)	—	—
B 226897	—	174746 (3)	171757 (6)	159872 (4)
C 222411	—	179230 (6)	176244 (5)	—
Supermultiplet due to the transition $5p \rightarrow 5s$				
	$5p^3P_0$ 188103.6 2676.6	$5p^3P_1$ 185427.0 2567.2	$5p^3P_2$ 182859.8	$5p^1D_2$ 177127.0
$5s^3P_0$ 224271	34886.4 (2)	38843.2 (3)	40130.1 (5)	45862.9 (3)
3P_1 222990		37563.0 (4)		
3P_2 218302		32872.4 (3)		
$5s^1P_1$ 215856		—		
	—	—	35439.6 (5)	38730.2 (7)

the chief evidence for the correctness of the identification. The identification of this ground multiplet receives additional support by the location, in the quartz region, of the super-multiplet due to the transition $5p \rightarrow 5s$ of the running electron.

According to the scheme proposed by S. C. Deb⁽²⁾ the intervals of the $5s^3P$ term

are $5s^3P_0-5s^3P_1 = 506$; and $5s^3P_1-5s^3P_2 = 1093$ so that $5s^3P_0-5s^3P_2 = 1599 \text{ cm}^{-1}$, a value less even than that of Ge I. Such an abnormally low value appears to be improbable from the following table in which the intervals $5s^3P_0-5s^3P_2$ of Ge I-like spectra are given together with the screening constants.

Table 5

Element	$5s (^3P_0-^3P_2) = \delta\nu$	$Z-s$	s
Ge I	1669	16.36	15.64
As II	2777	18.58	14.42
Se III	4114	20.49	13.51
Br IV { (writers)	5970	22.49	12.51
{ (Deb)	1599	16.18	18.82

Perhaps it might be suggested that the regular doublet law is often found to be inapplicable to the intervals of terms other than those of the deepest ($4p^3P$ in this case). But it would be difficult to assume that such abnormality occurs suddenly at Br IV. There is yet another interesting sequence which confirms the value of 5970 cm^{-1} for the interval $5s^3P_0-5s^3P_2$ of Br IV. According to Goudsmit's theory of multiplet separations this interval should be slightly less than the limit $mp^3P_{\frac{3}{2}}-mp^3P_{\frac{1}{2}}$ of the next higher ion, since the levels $5s^3P_{0,1,2}$ and $5s^1P_1$ are derived by the addition of an s electron to the ion in the 3P state. This rule is found to hold good remarkably well in almost all the spectra⁽⁵⁾ of the type under consideration, as is shown in table 6.

Table 6

	C I	N II	O III	F IV	Si I	P II	S III	Cl IV
$ms (^3P_0-^3P_2)$	60.1	167.96	375.3	618	271.93	528.1	449.7	1446
$(m+1) s (^3P_0-^3P_2)$	—	170.70	373	—	282.9	546.8	924.2	—
$(m+2) s (^3P_0-^3P_2)$	—	173.4	—	—	284.4	—	—	—
Lt. $mp (^3P_{\frac{3}{2}}-^3P_{\frac{1}{2}})$	C II	N III	O IV	F V	Si II	P III	S IV	Cl V
	64.0	174.4	387	—	287	566	950	1492

	Ge I	As II	Se III	Br IV
$ms (^3P_0-^3P_2)$	1666.1	2778	4114.1	5970
$(m+1) s (^3P_0-^3P_2)$	1740.2	—	4354.3	—
$(m+2) s (^3P_0-^3P_2)$	1764.9	—	—	—
Lt. $mp (^3P_{\frac{3}{2}}-^3P_{\frac{1}{2}})$	Ge II	As III	Se IV	Br V
	1768	2940	4376	6085

The analysis of Br IV suggested by Deb, which is essentially based on the identification of the interval 1599 cm^{-1} for $5s^3P_0-5s^3P_2$, appears therefore to be erroneous from the above considerations. A further test of the correctness of the identification will be afforded by the location of the remaining levels of the $5p$ configuration, namely 3D , 3S , etc.

With a knowledge of the characteristic intervals of the $4p^3P$ term, obtained by

the writers, it has been possible to locate, though only partially, the terms due to the $4d$ and the sp^3 configurations of the atom. All the combinations so far obtained are shown in table 4. There can be no doubt as to the reality of these levels that have been discovered for they have been based on very careful measurement of the lines, which could be confidently assigned to Br IV. Owing to the abnormally large values of the separations involved, however, the allocation of the levels to the various terms of the respective states of the atom cannot be considered final.

It may be pointed out that the $4d^3D$ term is regular in the spectra of As II and Br IV while in Ge I and Se III it shows partial inversion. The absence of the combination $4p^3P_0-4d^3P_1$ may throw some doubt on the identification of the $4d^3P_1$ level; but it is significant that this combination is missing in Se III also. The lines $\nu\nu$ 175706, 166318 and 165088 did not form pairs giving any characteristic separations, and hence the assignment of these lines to the combinations suggested in the above scheme is to be regarded as tentative.

§ 3. TERM VALUES

Term values of Br IV are calculated from the two members of the mp^3P series that have been identified in the present work thus:

$$5s^3P_2-4p^3P_2 = -180350,$$

$$5s^3P_2-5p^3P_2 = 35439.6; \text{ from which } 5s^3P_2 = 218302,$$

and the deepest term $4p^3P_0 = 404890 \text{ cm}^{-1}$ yielding a value of about 50.0 volts for the ionization potential of the trebly-ionized bromine atom. The terms and their values are listed in table 7.

Table 7. Term values of Br IV

Term	Term value	Term	Term value
$4p^3P_0$	404890	$4d^3P_2$	228204
$4p^3P_1$	401643	b	226897
$4p^3P_2$	398653	$4d^3P_0$	225937
$4p^1D_2$	386775	$4d^3P_1$	224312
a	265711	$5s^3P_0$	224271
$sp^{33}D_1$	250993	$5s^3P_1$	222990
$sp^{33}D_2$	242940	c	222411
$sp^{33}P_2$	237322	$5s^3P_2$	218302
$sp^{33}P_1$	236903	$5s^1P_1$	215856
$sp^{33}P_0$	236555	$5p^3P_0$	188103.6
$4d^3D_1$	235980	$5p^3P_1$	185427.0
$4d^3D_2$	234865	$5p^3P_2$	182859.8
$sp^{33}D_3$	232332	$5p^1D_2$	177127.0
$4d^3D_3$	232009		

In table 8 a list of all the classified lines, together with the classifications suggested in the present work, is given.

Table 8. Classified lines of Br IV

λ	$\nu_{\text{vac.}}$	Classification	$\lambda_{\text{vac.}}$	$\nu_{\text{vac.}}$	Classification
3041.18 (3)	32872.4	$5s^3P_2-5p^3P_1$	607.02 (6)	164740	$4p^3P_1-sp^3P_1$
2865.61 (2)	34886.4	$5s^3P_1-5p^3P_0$	605.74 (5)	165088	$4p^3P_1-sp^3P_0$
2820.87 (5)	35439.6	$5s^3P_2-5p^3P_2$	603.65 (5)	165659	$4p^3P_1-4d^3D_1$
2661.40 (4)	37563.0	$5s^3P_1-5p^3P_1$	601.26 (10)	166318	$4p^3P_2-sp^3D_3$
2581.19 (7)	38730.2	$5s^1P_1-5p^1D_2$	600.08 (8)	166644	$4p^3P_2-4d^3D_3$
2573.68 (3)	38843.2	$5s^3P_0-5p^3P_1$	599.60 (8)	166778	$4p^3P_1-4d^3D_2$
2491.14 (5)	40130.1	$5s^3P_1-5p^3P_2$	592.03 (9)	168910	$4p^3P_0-4d^3D_1$
2179.77 (3)	45861.9	$5s^3P_1-5p^1D_2^*$	586.60 (10)	170447	$4p^3P_2-4d^3P_2$
$\lambda_{\text{vac.}}$	$\nu_{\text{vac.}}$		585.08 (9)	170918	$4p^1D_2-5s^1P_1$
735.66 (10)	135933	$4p^3P_1-a$	582.22 (6)	171757	$4p^3P_2-b$
718.50 (10)	139179	$4p^3P_0-a$	576.57 (10)	173440	$4p^3P_2-4d^3P_1$
677.24 (5)	147658	$4p^3P_2-sp^3D_1^\dagger$	573.59 (8)	174340	$4p^3P_2-4d^3P_1$
663.80 (10)	150648	$4p^3P_1-sp^3D_1$	572.26 (3)	174746	$4p^3P_1-b$
663.19 (2)	150787	$4p^1D_2-4d^3D_1$	569.27 (6)	175663	$4p^3P_2-5s^3P_1$
658.28 (1)	151912	$4p^1D_2-4d^3D_2$	569.13 (10)	175706	$4p^3P_1-4d^3P_0$
649.78 (6)	153898	$4p^3P_0-sp^3D_1$	567.40 (5)	176244	$4p^3P_2-c$
646.15 (1)	154762	$4p^1D_2-4d^3D_3$	563.92 (8)	177331	$4p^3P_1-4d^3P_1$
642.22 (10)	155710	$4p^3P_2-sp^3D_2$	563.79 (9)	177372	$4p^3P_1-5s^3P_0$
630.12 (10)	158701	$4p^3P_1-sp^3D_2$	559.74 (9)	178653	$4p^3P_1-5s^3P_1$
625.50 (4)	159872	$4p^1D_2-b$	557.94 (6)	179230	$4p^3P_1-c$
619.86 (7)	161328	$4p^3P_2-sp^3P_2$	554.48 (8)	180350	$4p^3P_2-5s^3P_2$
618.25 (5)	161748	$4p^3P_2-sp^3P_1$	549.75 (9)	181900	$4p^3P_0-5s^3P_1$
610.55 (2)	163786	$4p^3P_2-4d^3D_2$	545.43 (5)	183341	$4p^3P_1-5s^3P_2$
608.56 (8)	164322	$4p^3P_1-sp^3P_2$	538.25 (2)	185787	$4p^3P_1-5s^1P_1$

* From Vaudet's list⁽⁶⁾.

† Coincidence with low stage line.

§ 4. ACKNOWLEDGMENT

It is a pleasure to thank Dr K. R. Rao for kindly placing his plates in the Schumann region taken with the Seigbahn vacuum spectrograph at our disposal and for many helpful suggestions during the course of the work.

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A METHOD FOR THE MEASUREMENT OF THE THERMAL DIFFUSIVITY OF POOR CONDUCTORS

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ABSTRACT. A new method of determining the thermal diffusivity of poor conductors is described. An irregularly shaped block may be used provided that it has a fairly large plane surface. Temperature-observations are made at two points within the block either by embedding thermocouples or by inserting them between cut surfaces. Small temperature-intervals (less than 10° C.) are used and considerable liberty of experimental conditions is afforded. Only a distance and quantities proportional to the temperature-changes at the two points need be measured. The method has been developed for use with wood, but results are given for a block of cast sulphur and several other common materials.

§ 1. INTRODUCTION

A METHOD was required for determining for wood the thermal diffusivity or the constant h^2 in the diffusion equation

$$\partial\theta/\partial t = h^2 \cdot \partial^2\theta/\partial x^2.$$

Thermal diffusivity is an important property of wood, more important perhaps than its conductivity, since wood is often used to insulate against temperature-changes rather than against a steady flow of heat. Moreover, the coefficient of diffusivity is used in calculations involved in such processes as seasoning, sterilization against beetle attack, impregnation and the glueing of veneers and plywood.

The method had to satisfy certain requirements introduced by the nature of the material ultimately to be investigated. The chief of these were (1) that the duration of the experiment should be short in order that movement of moisture, if any occurred, should not be appreciable; (2) that moderately large test pieces should be employed in order that the data obtained might be useful in practice, for determinations of the thermal conductivity of poor conductors such as wood have often involved thicknesses small enough to be comparable with the coarse structure of the specimens; and (3) that only small intervals of temperature should be used, since a fairly large variation of the coefficient with temperature was expected.

The Fourier diffusion equation has been applied to many particular cases, most of which have, at some time or other, formed the bases of experimental methods for determining either conductivity or diffusivity. The case of the semi-infinite solid with one plane boundary seemed the most easily realized and was therefore adopted.

Reference to literature shows that this case has been used by Kirchhoff and Hansemann*, Schulze† and Gruneisen‡, all of whom worked on metals.

A great disadvantage of the method used by Kirchhoff and Hansemann and by Schulze was the assumption that the plane boundary was instantaneously brought to the temperature of a stream of water passing over it. Their measurements also depended on an exact knowledge of the time at which this occurred. Gruneisen evaded these assumptions by fitting his readings to theoretical ones by means of a previously calculated table. Although Gruneisen claims that his method does not require a knowledge of the temperature of the boundary, this table is calculated by means of an arbitrary constant which is in fact proportional to the temperature of the boundary. His paper does not indicate how this constant is chosen.

The present method differs from Gruneisen's in providing a graphical means of rapidly carrying out the fitting process, including a unique choice of the figure corresponding to Gruneisen's arbitrary constant. In addition Gruneisen's presentation of the theory is simplified. The method possesses, in common with Gruneisen's, the following advantages: (1) It does not necessitate a knowledge of the temperature of the heated face; (2) it does not necessitate exact registration of the zero of time; (3) only the distances apart of the temperature-measuring instruments are required, not their distances from the plane boundary; (4) quantities proportional to temperature-changes, not temperatures themselves, are measured; (5) the temperature-interval used is small (less than 10° C.).

Because of the inhomogeneity of wood and because precise measurements of its diffusivity by other methods are not available for comparison, the method has been tested initially on sulphur in the rhombic form. Sulphur has the advantages of being non-hygroscopic, and pure and consequently reproducible; it has, moreover, a diffusivity comparable with that of many woods. Further, values of the diffusivity can be calculated from available data on the conductivity, density and specific heat.

§ 2. THEORY OF THE METHOD

The block extends to infinity in all directions except the negative x direction. The plane $x = 0$ is the heated face. The uniform initial temperature of the block is taken as the zero of measurement.

The solution of the Fourier diffusion equation

$$\partial\theta/\partial t = h^2 \partial^2\theta/\partial x^2 \quad \dots\dots(1),$$

with the conditions

$$\theta = 0, \text{ when } t = 0,$$

$$\theta = \theta_0, \text{ when } x = 0,$$

is

$$\theta = \frac{2\theta_0}{\sqrt{\pi}} \int_0^\infty e^{-\beta^2} d\beta \quad \dots\dots(2) \S,$$

where $q = x/2h\sqrt{t}$; t is time and h^2 the diffusivity.

* *Wied. Ann.* 9, 1 (1880).

† *Ibid.* 66, 207 (1898).

‡ *Ann. d. Phys.* 3, 43 (1900).

§ See, for instance, Ingersoll and Zobel, *Mathematical Theory of Heat Conduction*, p. 78.

Now suppose that a temperature-rise is observed at x_1 which can be represented by

$$\theta = \frac{2\theta_0}{\sqrt{\pi}} \int_{q_1}^{\infty} e^{-\beta^2} d\beta \quad \dots\dots(3),$$

where $q_1 = x_1 + S/2h\sqrt{(t+T)}$.

Then to get an expression for the temperature rise at x_2 (where $x_2 > x_1$) we require to solve equation (1) with the conditions

$$\left. \begin{aligned} \theta &= 0 \text{ when } t = 0 \\ \theta &= \frac{2\theta_0}{\sqrt{\pi}} \int_{q_1}^{\infty} e^{-\beta^2} d\beta \text{ at } x = x_1 \end{aligned} \right\}.$$

Now

$$\theta = \frac{2\theta_0}{\sqrt{\pi}} \int_q^{\infty} e^{-\beta^2} d\beta,$$

where $q = (x + S)/2h\sqrt{(t+T)}$ is a solution of equation (1) satisfying these conditions so that it is the solution required for all points such that $x > x_1$. Therefore when $x = x_2$

$$\theta = \frac{2\theta_0}{\sqrt{\pi}} \int_{q_2}^{\infty} e^{-\beta^2} d\beta \quad \dots\dots(4),$$

where $q_2 = (x_2 + S)/2h\sqrt{(t+T)}$.

The three quantities θ_0 , S , and T allow the fitting of the actual temperature-rise at x_1 to a theoretical one of the form required. In effect, they state that temperature-rises at x_1 and x_2 such as those observed would have been caused by the instantaneous establishment from a time $-T$ of a constant temperature θ_0 at a plane distant $-S$ from the plane $x = 0$.

Since $1/q^2$ or $4h^2(t+T)/(x+S)^2 \quad \dots\dots(5)$

is a linear function of t for a given value of x , straight lines should result if $1/q^2$ be plotted against t . The slopes of the lines for x_1 and x_2 are respectively

$$m_1 = 4h^2/(x_1 + S)^2 \text{ and } m_2 = 4h^2/(x_2 + S)^2$$

so that

$$h^2 = (x_2 - x_1)^2 \cdot (m_1 m_2) / 4 (m_1^{\frac{1}{2}} - m_2^{\frac{1}{2}})^2.$$

For any one experiment only one value of θ_0 will give straight lines for these plots, so that it can be obtained by trial. S and T do not have to be chosen since they are involved in the lines so chosen, S in the slope and T in the intercept on the time axis. Thus the temperature conditions at the plane $x = 0$ are not brought into the calculation at all.

The one essential condition of the experiment is that the temperature-rise at x_1 should be represented by a curve of the family of equation (1), a condition which can be closely complied with experimentally in many different ways—as many ways as there are pairs of values of S and T . Actually, in the work to be described, it was found sufficient to allow the plane $x = 0$ to heat up under hand control, to a predetermined temperature, the process taking from one-half to two minutes, and then to come under automatic control and retain constant temperature while temperature-readings within the block were taken. A few trials soon indicated a schedule of heating which would satisfy the conditions of the theory.

§ 3. EXPERIMENTAL ARRANGEMENT

In casting the block of sulphur special precautions were necessary in order to avoid the consequences of the shrinkage which takes place on solidification. Electric heating elements on the metal lining to the mould enabled the cooling of the casting to be controlled. The block used measured 5 in. \times 5 in. \times 5 in. and had four thermocouples cast in position on the axis. The cross-section was so chosen in relation to the depth of the lowest thermocouple that sideways conduction was negligible according to a theoretical investigation by Peirce and Wilson*.

The specific gravity of the casting, as determined from about two cubic inches cut near the thermocouples, was 1.93. The specific gravity of rhombic sulphur is 2.07, but this cannot be attained in a casting since molten sulphur sets first in the monoclinic form (the density of which is 1.96) and afterwards changes slowly into the rhombic form, leaving a slightly porous casting.

Blocks of the other materials used were made with the same dimensions. In order to avoid difficulties of drying, the wooden test pieces were only 1 in. square by 6 in. long but were surrounded by guard rings of the same material. The thermocouples (made of foil and covering the whole cross-section) were inserted by slicing the inner test piece. The block and its heating plate, together with asbestos boards at top and bottom, were then placed in a clamp holding all together with a light pressure. A liberal covering of cotton wool round the sides served to minimize any temperature-fluctuations which might be introduced from the sides.

The leads from the thermocouples were taken to a mercury-cup switch-box and thence to a Tinsley vernier potentiometer. Since, in the use of the potentiometer, transits of the galvanometer-spot across the zero were timed for certain settings of the dials, it was an advantage to keep the resistances of the thermocouple circuits as low as possible. The movement of the spot was then more rapid and the timing of the transits more definite. Over the small range used in any one experiment (less than 10° C.) the variation of thermal e.m.f. with temperature could be taken as linear. However, in order that the initial temperatures might be known, the couples were calibrated at the National Physical Laboratory.

The heating plate consisted of a 400-ohm 220-volt asbestos-woven resistance mat clamped between two 16-s.w.g. sheets of copper. Five copper-eureka thermocouples in series were also placed between the plates, but insulated from the mat, to actuate the control.

Two resistances in series, figure 1, enabled the heating-current to be adjusted, first for rapid initial heating at various oven temperatures, and afterwards for slow heating with about 10 watts while the control was in operation. Experience indicated good settings for each of these conditions.

The control is represented diagrammatically in figure 1. The whole of the controlling relay was actuated from d.-c. 220-V. mains.

* *Proc. Am. Acad.* 34, 1 (1899).

§ 4. THE METHOD

The block under test was placed in the oven and raised to the temperature at which its diffusivity was to be measured. The control for the plate was set about 10°C. higher. When the block had attained a uniform temperature, as indicated by the thermocouples, the heating-plate and a stop-watch were switched on. As the plate neared its controlled temperature, indicated by the mirror galvanometer, the external series resistance was smoothly altered until, at the desired controlled temperature, slow heating or cooling took place according to the position of the relay. After an interval of 5 min. from the commencement of heating, temperature-readings were begun. Each couple was connected to the potentiometer in turn and

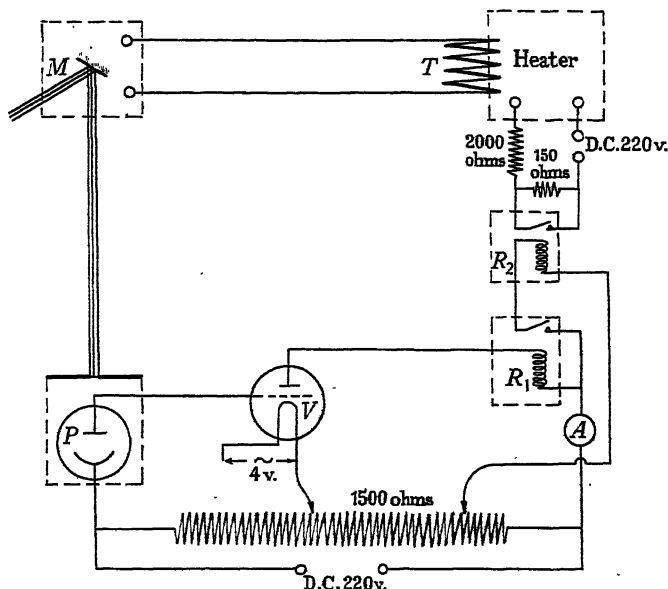


Figure 1. Apparatus for temperature-control of heating-plate. *P*, photocell; *V*, valve (Marconi PX4); *A*, milliammeter; *R*₁, relay (5 mA. Post Office); *R*₂, relay (30 mA.); *M*, mirror-galvanometer (Tinsley).

readings were taken at intervals over a period of 20 min. Preliminary work had shown that no appreciable rise of temperature took place at the far end of the block during the total time of the experiment, so that for the purposes of this experiment the block could be considered semi-infinite. As a check on the readings a smooth curve was fitted to the microvolts plotted against time for each couple. These curves also assist in choosing the value of θ_0 which enters into equation (3).

With a value of θ_0 chosen in this way, q^{-2} was plotted against t . The readings of the uppermost couple were plotted on this special scale for several values of θ_0 until the value which gave a straight line for the plot was found. This is not difficult, for, starting with too large a value of θ_0 , we obtain a line concave to the time axis; if the chosen value of θ_0 is decreased, the line becomes less concave, then straight, and afterwards more and more convex to the time axis. The choice of values of

S and T is automatically included, for only one value of θ_0 will give a straight line, and S and T determine respectively the slope and intercept on the time axis of that line. In practice a very few trials gave the desired value of θ_0 . This value was then used to plot the straight lines for the other, lower couples. Any departure of these from straightness indicates that the conditions of the theory have not been exactly fulfilled. All the plotting was done on a drawing-board measuring 30 in. \times 24 in. A steel rule divided into tenths of an inch was fastened to one edge and served as the time scale, and a special T square gave the scale of q^{-2} , equation (5). The divisions on this square are marked with values of θ/θ_0 from 0 to 0.65, but the distance of any mark Δ from the zero is proportional to q^{-2} , where q and ∞ are those limits of the definite integral of equation (2) for which it has the value Δ . A table of values of q and Δ appears in the *Mathematical Theory of Heat Conduction* by Ingersoll and Zobel and, more conveniently with equal intervals of Δ , in *Tables for Statisticians and Biometricians* by Pearson (part II, table II). In the last-named publication, values of the argument require to be multiplied by 2 for the purpose of this paper.

Figure 2 is an example of a set of these straight lines from an actual experiment. The temperature-rise in microvolts for couple 1 is shown in the same diagram.

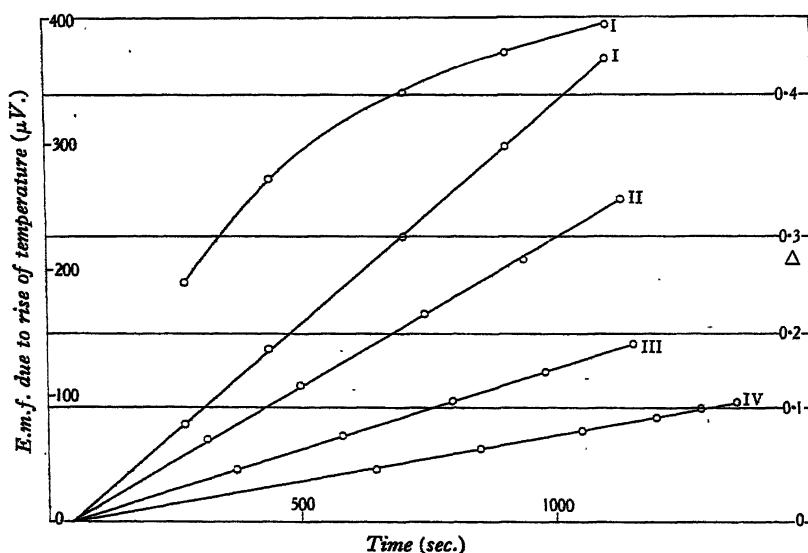


Figure 2. The upper curve shows the potential difference ($\mu V.$) corresponding to the actual temperature-rise at couple 1. Straight lines I to IV are for couples 1 to 4 on a special scale.

§ 5. RESULTS

The results of individual experiments at various initial temperatures are set out in table 1. As is usual in determinations of diffusivity, the measurement of distance contributes the greatest risk of error in the result. For this reason the results calculated from couples 1 and 4, involving the largest distance, are included in the table. Only one pair of couples is actually necessary; the others were provided as a check.

Table 1. Thermal diffusivity of rhombic sulphur

(a) Calculated from couples 1 and 2. (b) From couples 1 and 4.

Temperature (°C.)	29.8	27.8	26.8	28.3	27.8	28.0	75.0	75.0	75.1	74.6
$h^2 \times 10^4$ (c.g.s. units)	(a)	16.8	17.0	16.8	17.0	16.7	17.3	15.3	14.7	15.1
	(b)	16.4	17.3	17.3	16.6	16.5	17.2	14.8	13.7	14.9

Inspection of the graphs showed that their results were not so reliable as those from the uppermost pair of couples. In the case of the sulphur block, the measurement of distance was made by means of a travelling microscope. The distance measured was that between the uppermost surfaces of the beads of the couples. There are no determinations of thermal diffusivity of sulphur for comparison, but by using separate values of specific heat and conductivity given by different observers, it is possible to calculate a figure; though, of course, it has the drawback that the constituent determinations were not made on the same material.

In table 2 the observed values of diffusivity are compared with values calculated from conductivities obtained by Kaye and Higgins* and by Green†. The calculation uses specific heats obtained by interpolation from Wigand's‡ results. The density was assumed to be 1.96 in the case of the first-named results; for the others it was known to be 1.94.

Table 2. Comparison with calculated values

(a) Kaye and Higgins. (b) Green.

Temperature (° C.)	$k \times 10^3$ (c.g.s. units)		Specific heat*	$h^2 \times 10^4$ (c.g.s. units)		
	(a)	(b)		Calculated		Observed†
				(a)	(b)	
20	0.650	0.615	0.1716	19.3	18.5	17.2
40	0.613	0.602	0.1722	18.2	18.0	16.4
60	0.581	0.588	0.1731	17.1	17.5	15.6
80	0.558	0.570	0.1742	16.3	16.8	14.8

* Interpolated from Wigand's values.

† Interpolated from mean values of table 1, column (a).

The lowness of the observed as compared with the calculated values cannot be attributed to any difference of density, for Green's results show that the density and conductivity of sulphur change approximately in the same proportion, for a small change at least, so that the diffusivity, involving as it does the quotient of conductivity and density, is practically unaltered by a change of density.

The diffusivities of various other substances have been measured by this

* *Proc. R.S. A*, 122, 633 (1929).

† *Proc. Phys. Soc.* 44, 295 (1932).

‡ *Ann. d. Phys.* 22, 64 (1907).

method but, their constitution being indefinite, comparison with values calculated from published values of density, conductivity and specific heat would not be expected to be very close. The comparison is made in table 3.

Table 3. Thermal diffusivities

Substance	$k \times 10^3$ (c.g.s. units)	Specific heat	Density	$h^2 \times 10^4$		Observed density
				Calculated	Observed	
Oak*	0.28†	0.33‡	0.60†	14.1	18	0.64
Oak	0.47§	0.33	0.82§	17.4		
Balsa¶	0.11†	0.33	0.10†	33.4	20	0.16
Balsa	0.13§	0.33	0.14§	28.1		
Sand, dry	0.78§	0.19**	1.52§	27.0	24	2.2
Glass, plate	1.78§	0.16**	2.49§	44.7	40	2.5
Plaster of Paris (cast)	0.7††	0.26‡‡	1.2‡‡	22.4	18	1.1
Paraffin wax	0.60§§	0.69**	0.9**	9.7	6.5	—

* Tangential flow, 14 per cent moisture (based on dry weight).

† Griffiths and Kaye. *Proc. R.S. A*, 104, 73 (1923).

‡ Dunlap. *U.S. Dept. of Agric.*, Bull. No. 110 (1912).

§ *Am. Soc. Ref. Eng. Circ.* No. 1 (1924).

¶ Tangential flow, 13 per cent moisture (based on dry weight).

** Kaye and Laby. *Physical and Chemical Constants*.

†† Lees and Chorlton. *Phil. Mag.* 41, 495 (1896).

‡‡ *International Critical Tables*, V, 99 and II, 123.

§§ Lees. *Phil. Trans.* 183, 481 (1892).

§ 6. ACKNOWLEDGMENTS

Thanks are due to Sir Ralph Pearson, C.I.E., LL.D., F.L.S., Director of the Forest Products Research Laboratory, for permission to publish this paper, and to Mr W. Barkas, M.Sc., in charge of the Section of Physics, for much helpful advice and criticism.

DISCUSSION

Dr EZER GRIFFITHS. I am much interested in the paper, as I have been concerned with the measurement of the diffusivity of the ground. I used an electrically heated sphere buried in the ground with thermocouples located at definite distances from the centre. The heat-supply was so arranged that the temperature of the surface of the sphere followed a sinusoidal curve; this simplified the mathematics required in calculating the diffusivity. The value was checked by independent determinations of the conductivity, the specific heat, and the density, from which the diffusivity was calculated.

I do not think sulphur is a suitable material for the author to use in checking the method as a cast block would have different properties in various directions. Possibly a substance like pitch would be better.

674.03:581.81

MEASUREMENT OF THE CELL-SPACE RATIO IN WOOD BY A PHOTOELECTRIC METHOD

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ABSTRACT. A method for measuring the cell-space ratio, or proportion of void space, in wood depends on measuring, by photoelectric means, the amount of light passing through a stained microsection of the wood. A correction for the amount of light penetrating the stained cell-wall is necessary. Comparisons are made between the results obtained by this method and those obtained by the use of a Shand's micrometer, and the conclusion is drawn that the photoelectric method is the more accurate and very much the more rapid. A description of the photoelectric amplifier is given.

§ 1. INTRODUCTION *

A KNOWLEDGE of the percentage of void space, or cell-space ratio, of a wood is essential to the solution of certain problems concerning its structural and mechanical properties, and investigations at present proceeding at the Forest Products Research Laboratory have shown the desirability of a simpler and quicker method than the one in general use.

The common method of measuring the cell-space ratio is to traverse the cross-section of the wood under a microscope with a Shand's micrometer, measuring the total distances across the walls and voids separately. Several traverses are made along lines truly representative of the differences in cell-growth, but the figures obtained for the cell-space ratio are only reproducible to within about ± 5 per cent. Moreover, since the diameters of the cells vary from about 0.3 mm. for large vessels down to 0.01 mm. or less for small fibres, the operation is always tedious, especially where large areas are to be measured or where the cells are very small (as for instance in the fibres of ash), and in the latter instance the accuracy must suffer since the width of the image of the micrometer pointer may be comparable with that of the diameters of the smallest fibres.

No comparison seems hitherto to have been made between the results obtained with the Shand's micrometer and those obtained by any independent method, but a paper entitled "Note on the combined use of the photoelectric cell and the projection microscope*," by Savage and Jamieson, gave an indication of the possibilities of using a light-sensitive cell as an alternative method. The authors of that paper measured the average size of certain spores, stained red and mounted in jelly, by projecting a magnified image of a known number of the spores on to

* *Canadian J. of Res.* 3, 322-6 (1930).

a photoelectric cell and comparing the deflection of a sensitive galvanometer with that given by a clear slide. The chief sources of error here lie in assuming that the photocell is insensitive to the light transmitted by the stained bodies, and in the unreliability of measurements made by galvanometer deflections.

This method was tried at the Forest Products Research Laboratory for the measurement of the cell-space ratio, but it soon became evident that the inherent errors were too large to allow of accurate results and that a correction for the amount of light transmitted by the stain would need to be made.

§ 2. THEORY

For the measurement of cell-space ratio of woods, since the ratio of void area to total area in a transverse microsection is equal to the ratio of void volume to total volume in the material in bulk, a principle similar to that used by Savage and Jamieson in the case of the stained spores may be followed. If a section could be stained absolutely black then the cell-space ratio would be simply the ratio of the light transmitted by the section to the total light transmitted by an equal clear area. In practice a black stain is not obtainable, but if the transmission of the stained wall is known a simple correction may be applied.

Let Q_0 , Q_1 and Q_2 denote the quantities of light transmitted respectively by equal areas of the clear portions of the slide, of the stained cell walls, and of the section as a whole. Then, if we denote the cell-space ratio by A , we have

$$Q_2 = AQ_0 + (1 - A)Q_1.$$

Since for a vacuum photocell working at saturation potential the current is proportional to the total quantity of light entering the cell, we may write

$$A = \frac{Q_2 - Q_1}{Q_0 - Q_1} = \frac{C_2 - C_1}{C_0 - C_1},$$

where C_0 , C_1 and C_2 are the currents corresponding to the quantities Q_0 , Q_1 and Q_2 respectively.

For convenience the values of Q_1 and Q_2 are expressed throughout the paper as percentages of Q_0 , and A as a percentage of the area of the section under consideration.

This formula requires a knowledge of the transmission ratio, Q_1/Q_0 , of the stain on the cell wall. It is not feasible to magnify the image sufficiently for a portion of the cell wall to cover the aperture of the photocell and thus to measure Q_1/Q_0 directly, because the light-intensity would be too low. The depth of stain on the cell wall must therefore be matched visually with one of a graded series of filters of the same stain by means of comparison microscopes at equal magnifications, each being illuminated at equal intensity by the light used in the photometer. The transmission Q_1/Q_0 of the filter chosen may then be measured on the photometer under the same conditions as is the transmission of the microsections.

§ 3. APPARATUS

(i) *The wood sections* used were about 1 cm. square and cut to a thickness of 15 μ . The use of a thicker section was considered undesirable, because any inaccuracy in cutting perpendicular to the grain meant that light would pass obliquely through the cell spaces so that a portion of the void area would be eclipsed, and the thicker the section the greater would be the amount of light eclipsed. In most woods, too, the cells are not all strictly parallel; for instance, the fibres are slightly inclined in passing round a medullary ray. The sections were stained in a concentrated dye, washed in water, air-dried without heat and mounted in Canada balsam under a cover slip. Since the slide, mounting-medium, and cover slip all absorb or reflect an appreciable amount of light (about 10 to 15 per cent by measurement) the value of Q_0 must be measured through these. For this reason a long cover slip was used so as to leave, alongside the section, an equal clear area. The annual rings of the section were placed parallel to the edge of the slide, so that the area included in the rectangular aperture of the photocell would be representative of a definite growth-period in the wood-section.

(ii) *The matching-filters* were made by mounting, on a glass slide, a glass ring of internal diameter 2 cm. and thickness 1 mm. This was filled with an aqueous solution of the dye used as stain, and was closed with a 2.4-cm. cover slip. The whole was sealed with Canada balsam and dried slowly without heat. By varying the concentration of the dye, filters of any desired depth could be made and a graded series of about ten filters, transmitting from about 1 to 15 per cent of light, was prepared.

(iii) *Optical arrangement*, figure 1. The slide S carrying the microsection was mounted on the rising and racking front of a camera body from which the lens had been removed*. An image of S was focused by an $f/2.4$ camera lens L_3 on to a rectangular aperture A placed immediately in front of the photocell P . The shape of the aperture could be varied to suit the area under measurement. To enable the focus to be judged and the area for examination to be chosen, a mirror M was so fixed as to rotate about C into the light-path and thus turn the image on to the ground-glass screen G on which the area of A was marked out. In this way any portion of the section might be chosen. When the mirror was out of action it served to close the back of the screen G . The two portions between the section S and the mirror M were enclosed in bellows. By suitably spacing L_3 and S , any magnification between 1.4 and 8 could be obtained.

(iv) *Comparison microscopes*. For matching the depth of stain of the section with one of a graded series of filters, the comparison microscopes (M_1 and M_2 , figure 1) were set up and illuminated from B by the prisms P_1 and P_2 and a suitable system of lenses. The substage condensers of the comparison microscopes were removed and the light was concentrated in two nearly parallel beams by a system of lenses. These lenses were adjusted until the intensities of the two fields were

* A rotating mount for the slide, such that the growth rings in a crooked section could be aligned with the edge of the aperture A , would be an improvement.

equal when viewed, at the same magnification, with a clear portion of a slide on one microscope stage and a clear filter on the other. If the condensers are not removed, matching becomes impossible because the light passes through the slide in a flat cone and suffers a certain degree of concentration by refraction. Under a magnification of about 500 the colour of the cell walls was clearly seen and the matching filter could be chosen with considerable accuracy provided the staining was dark. If the stain is too light, different portions of the cell wall stain to different depths, and, further, for light stains the eye is much less sensitive than for deep stains to small differences in transmission between one filter and another. It has been found that the cell wall of most woods may be stained with methylene blue to pass only about 5 per cent of the sodium light. Above about 12 per cent the matching becomes unreliable for the reasons mentioned above.

§ 4. DEVELOPMENT OF METHOD

To test for the best illuminating colour and the best stain, the optical system in figure 1 was modified in such a way as to enable any narrow band of wave-lengths from the continuous spectrum of a 12-V. line-filament car lamp to be passed through a fine slit and used for illuminating the slide at *S*, the colour band being selected by rotating the prism through which the light passed.

For the purpose in view it was more important that the colour effects should be tested under the working conditions of figure 1 than that the actual values of the wave-lengths employed or their real intensities should be known. For this reason the spectrum was plotted out in terms of the rotation of the prism, while the response of the photocell to any colour was taken as a percentage of the maximum response recorded.

The response of the photocell to all parts of the continuous spectrum showed that this maximum response lay just in the infra-red and fell off rapidly towards the violet; the extreme infra-red was absorbed by the glass. In order that the photocell should not respond to invisible rays, which the eye could not match in the filters, a 2-inch glass cooling-tank was introduced and curves were taken for varying concentrations of CuSO_4 solution as percentages of the clear deflections. From this a $\frac{1}{2}$ to 1-per-cent concentration was chosen as the best for absorbing the infra-red without unduly reducing the intensity in the visible region.

The response of the cell to the continuous spectrum was seen at once to be very different from that of the eye, and in the yellow-to-red region the sensitivity of the cell increases, while that of the eye decreases, with increase in wave-length. Thus it was suspected that the visual matching of filters to the stained sections would be unreliable if even a slight change in the colour of the dye were to occur on staining the section, since this change might be in regions of the spectrum which, though affecting the photocell, would not be noticed by the eye. Trials showed this to be the case. Even when a very narrow band of colours in the orange was used both for matching and for measurement of transmission, the range of colour was sufficient to introduce these errors.

From this it was concluded that only a monochromatic source could, with safety, be employed in this method. Use was therefore made of the new Zeiss sodium-vapour lamp, while a methylene blue stain was chosen for the sections, since measurement showed that it possessed a strong absorption band in the region of the *D* lines. Since the intensity of other lines (e.g. of helium) in the spectrum of the lamp is very low, the prism and slit arrangement could be dispensed with, the final apparatus then taking the form shown in figure 1. The 1 per cent CuSO_4 cooling cell may be retained as a precaution, though the heat radiation from this lamp is much weaker than that from a filament bulb.

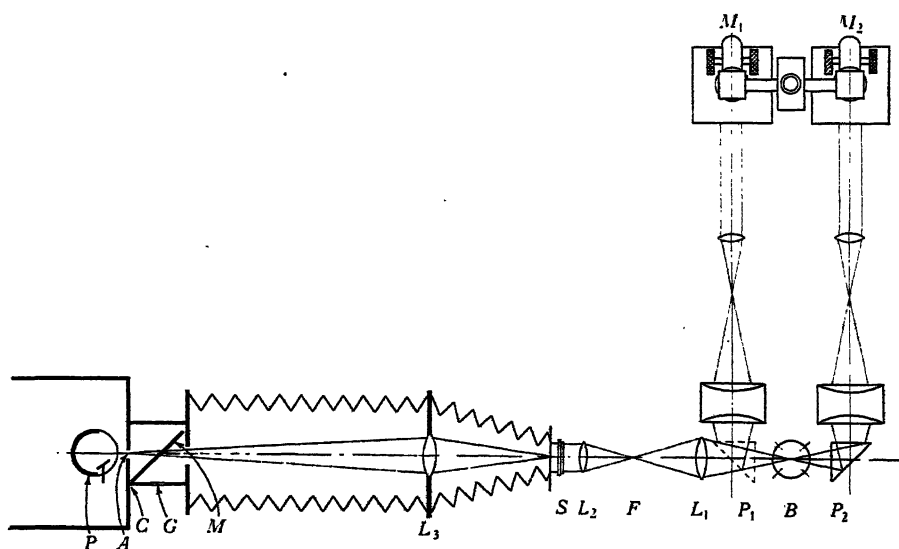


Figure 1. Final lay-out of apparatus.

§ 5. TEST OF METHOD

Since other uses to which the amplifier had been put* had shown that this part of the apparatus is reliable, provided that a constant source of illumination is used, no special tests were made upon it. Attention was therefore confined to tests of the method (i) for accuracy where personal judgment is not necessary in the choice of matching filter; (ii) for reproducibility of measurements on several microsections of identical cell-space ratio but different depths of stain; (iii) for agreement in the choice of matching filter made by several observers on the same microsections; (iv) for the significance of the differences obtained on microsections of different cell-space ratio. These tests are detailed below:

(i) First, to test the method in a case where the continuous filter is a perfect match, grids were cut from translucent papers such as are used for dark-room lanterns. The bars and clear spaces were each as nearly as possible 1 mm. wide.

* W. W. Barkas, "Notes on an optical method of measuring 'finish' on a planed wood surface," unpublished report, Forest Products Research Laboratory (1933).

The matching filter was, in this case, a continuous portion of the same material alongside the grid. The grids, after being mounted on a glass slide, were measured under a travelling microscope to determine the percentage of void space. Table 1 shows the results obtained with the photometer, at a low magnification, when an equal number of bars and spaces were included in the field of view:

Table 1. Percentage of void area of paper grid

Colour of grid	Light passed by		Void area, as measured by	
	paper	grid	photo-meter	direct measurement
Green	1.0	49	48.5	49.6
Red	7.0	55	50.7	50.9

This showed that the method is sufficiently accurate in the case of an ideally matched filter.

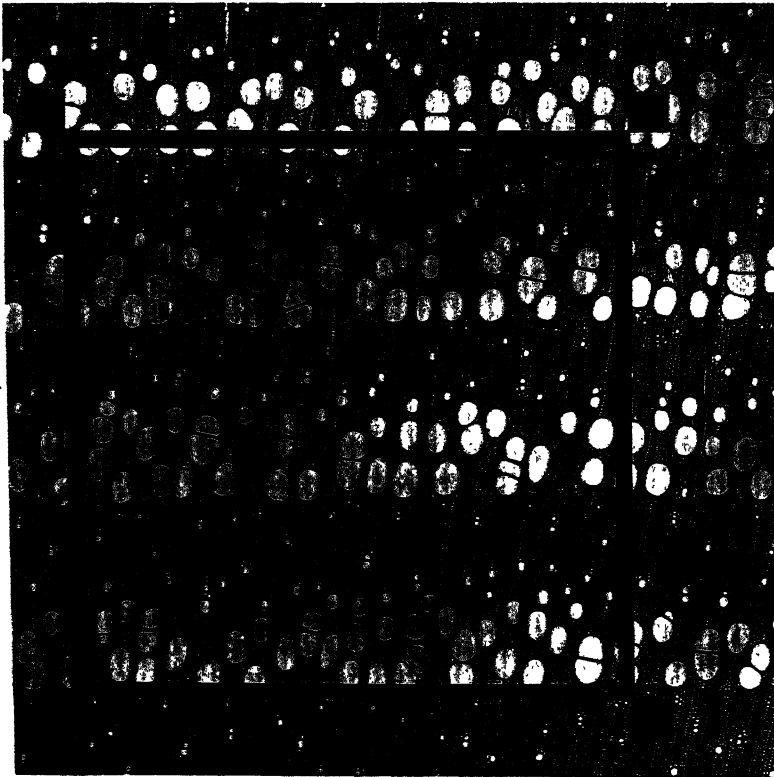


Figure 2. Test section of ash showing area measured (magnification 17.6).

The possibility that the light in passing through the fine holes in the section may be scattered outside the aperture of the photocell is not tested by this method.

Since no method suggested itself whereby a structure of *known* void area and translucence, having voids comparable in size with those of a wood section, might be constructed, the only check on the existence of such an error appeared to be the comparison of the value of the cell-space ratio obtained by means of the photometer with that given by some other independent method. This is dealt with in § 6.

(ii) Next, to test the accuracy of results obtained by matching, a set of 10 sections, 15 μ . thick, were cut successively from a sample of ash chosen for straight grain and even annual rings, figure 2. The total thickness of wood removed from the block was thus only 0.015 cm., so that no appreciable differences were to be expected between the average cell-space ratios of the individual sections. These sections were given identical treatment in mounting except for the depth of stain. The same square area, the side of which was exactly equal to the width of 3 annual rings, was chosen on each section, figure 2, and the magnification was set so that exactly this area and no more was included in the field of view. The photometer measurements were made immediately after matching to avoid possible errors due to fading.

Table 2. Comparison of cell-space ratios obtained in the case of identical sections having different depths of stain

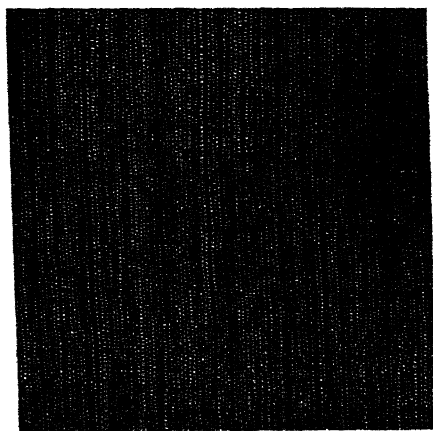
Section no.	Percentage transmission of filter	Percentage transmission of section	Cell-space ratio
Ash ... 1	(10 to 14) (say 12)	48.5	41.5
2	8	45	40
3	17	52	42.2
4	14	54	46.5
5	10	48	42.2
6	10	46	40
7	10	46	40
8	5	45	42.1
9	10	50	44.5
10	10	48	42.2
		Average	42.1
Scots pine 11	2	43	41.8

A set of six matching filters of methylene blue*, passing 2, 5, 8, 10, 14 and 17 per cent of the sodium light, was used.

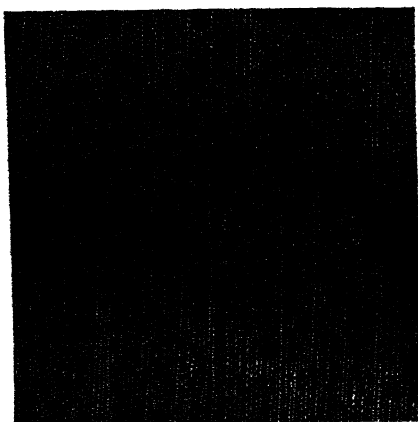
Above about 12-per-cent transmission the choice of matching filter becomes doubtful, and the choice for sections 3 and 4 was difficult for this reason. If these two are omitted on account of matching-errors the average becomes 41.6 per cent and the total scatter 4.5 per cent. This omission is justified since these sections were purposely prepared to cover a range of staining greater than would be

* These filters had been prepared for tests under prism illumination before the sodium vapour lamp had been introduced. Under monochromatic light a set of neutral grey filters would serve equally well and should not be so subject to fading.

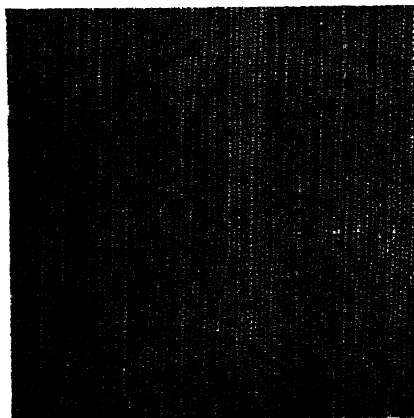
expected in practice, where the darkest stain is aimed at and the range, therefore, considerably smaller*.



Summer wood.



Late spring wood.



Early spring wood.

Figure 3. Test sections of *insignis* pine showing areas measured (magnification 17.6).

* It should be pointed out that the differences recorded in table 2 for the cell-space ratio are to some extent accounted for by the fact that the sodium-vapour lamp was running from the mains which were subject to sudden changes of load within the Laboratory. Had large-capacity h.-t. accumulators been available a better agreement would have been anticipated. Indeed previous comparison experiments, not recorded here, were carried out with the prism set up with a 12-V. car battery as described above, and proved that a constant source of illumination did give results which were individually more reproducible than was any one reading in table 2. In spite of this advantage the prism method was abandoned in favour of the sodium lamp because, for reasons explained on p. 548 above, the difficulty of matching under prism illumination made for poorer agreement between the values of the cell-space ratio for the separate sections. Moreover, persistent "storms" in the mains are easily observable on the photometer, and readings may be postponed till load-changes are a minimum, whereas the discrepancies under prism illumination, due to colour-changes in the stain, may pass quite unsuspected unless a large number of identical sections are prepared together for comparison. For routine work this is out of the question.

(iii) and (iv). As a test of the agreement between the judgment of match made by several observers, and of the significance of the differences between values obtained on sections having different cell-space ratios, the following results on *insignis* pine, table 3, may be quoted. In this case the values of the lightly stained sections have been omitted as unreliable, though those quoted are, on the whole, lighter than could have been obtained without difficulty.

Table 3. *Insignis* pine. Comparison of cell-space ratio for sections stained to medium depths and matched by observers X, Y and Z

Section no.	Q_2/Q_0	Transmission of matching filter				Cell-space ratio			
		X	Y	Z	Average	X	Y	Z	Average
Summer wood									
1	46	8	5	8	7	41	43	41	41.7
2	51	11	21	23	18	45	38	31.5	38.2
3	47	8	11	8	9	42	40	42	41.3
4*	43	8	5	5	6	38	40	40	39.3
Averages ...						41.5	40.3	38.6	40.1
Late spring wood									
1	67	5	9	11	8	65	63	62	63.3
2	67	8	7	9	8	64	64	63	63.7
3	65	8	8	8	8	62	62	62	62.0
Averages ...						63.7	63.0	62.3	63.0
Early spring wood									
1	70	5	9	11	8	68	67	65.5	67.5
2	71	8	7	9	8	68	68	68	68.0
3	68	8	8	8	8	65	65	65	65.3
Averages ...						67.0	66.6	66.1	66.9

A sample of *insignis* pine which had very wide annual rings was chosen. The sections were cut from a single ring-width and mounted as before. The magnification was increased so that three separate areas could be measured within this ring, one in the summer wood, one in the late spring wood, and one in the early spring wood, figure 3.

It will be seen that, except for the summer-wood portion of section 2, which is too lightly stained, the values of the cell-space ratio calculated for the separate observers agree to within 3 per cent. The differences between the values for the three areas chosen are also seen to be significant.

The tests given above show that the method may be relied upon to give consistent and significant results.

* The spring-wood portions of section no. 4 were found to be uneven in stain and were therefore rejected.

§ 6. COMPARATIVE TESTS

(i) The degree of reproducibility of the results having been established, it now became necessary to compare the results obtained by the photometric method with those found by other methods of which the one using Shand's micrometer is the most important. In order to do this, section 1 (table 2) was measured by an experienced observer who made three traverses on the Shand's micrometer. The values obtained were 54, 59 and 50 per cent. This result not only showed the large variations to be expected from this method but also suggested that these values might always be higher than those obtained with the photometer. A previous measurement on Scots pine (no. 11, table 2) gave a similar difference; the photometer gave 41·8 per cent and the micrometer 52·4 per cent (average of 3 observations). Two other observers measured this latter section (no. 11) by the micrometer and obtained similar values. It appeared therefore that the micrometer values were not the result of any personal bias on the part of the individual observer. Tests were therefore undertaken to decide which method gave the more accurate value, and possible causes of the discrepancy were investigated.

There were two main reasons for supposing that the photometer method was not at fault. Firstly, the measurements corresponding to cell-space ratio in the case of the paper grid, § 5 (i), gave true results. Secondly, if the accuracy of the correction were doubted the value of Q_2/Q_0 in table 2 would still have to be higher than the true cell-space ratio owing to the transmission of the stained cell walls. The transmissions Q_2/Q_0 of the sections as a whole were, however, all lower than the average obtained with the micrometer, nos. 3 and 4 being omitted, and their average (which is 48·2 per cent) was considerably lower.

A low value with the photometer could possibly be accounted for by stain having soaked out of the cell wall into the mounting-medium filling the cell spaces. On this assumption the transmission of the contaminated void spaces (which we may call Q_3) was calculated with the photometer values of Q_1 and Q_2 as before, the value A' of the cell-space ratio as measured on the micrometer being assumed to be correct. For section no. 1, table 2, we have

$$Q_2 = 41\cdot5; Q_1 = 12; A' = 54$$

so that $Q_3 = 67$ per cent. This means that one-third of the light falling on the void spaces must be stopped out by the contamination in the voids. Such a large contamination should be easily visible, but on careful comparison of the tint of the voids with that of the clear portion of the slide under the comparison microscopes, no difference could be observed between them. The explanation was therefore untenable. Another possible explanation of the lowest photometer value, namely that the light is scattered in passing through the section, has already been mentioned and is shown to be improbable as a result of the tests given in paragraph (iii) below.

(ii) To decide whether the system of traversing tended inherently to give a wrong result, a large number of circles of different known sizes were drawn on

a sheet of paper in as random a fashion as possible, so as to cover the sheet without overlapping. From their radii the area covered by the circles was calculated as 54.5 per cent of the area of the paper. Sixteen traverses were made by ruling fine lines in random directions and measuring intercepts. The total number of circles intercepted was 281, which is of the same order as the number of cells crossed on two annual rings. The final average obtained for 16 traverses was 56 per cent, showing a difference of 1.5 per cent, which is well within the limit of accuracy of the experiment. The addition of four more traverses did not appreciably alter this average value.

(iii) In order to obtain independent measurements of the cell-space ratio of the wood section, two methods were adopted. The first method consisted in projecting an enlarged image of section no. 11, table 2, onto millimetre-squared paper and computing the areas of separate cells from the number of millimetre squares covered by the images. The magnification being necessarily large, a single annual ring was measured by six separate projections of small areas spaced diagonally across the ring*. The results are shown in table 4, which also includes measurements on another wood as a check.

Table 4. Comparison of cell-space ratio by three methods

Section	Cell-space ratio as measured by		
	projection	photocell	Shand's method
Scots pine	39	42	52
Sycamore	30.7	31	44

It will be seen that the results are in better agreement with those of the photometric method than of Shand's method.

The other measurement of the cell-space ratio was made by fitting the Shand's micrometer on to a projection microscope and making the highly magnified image of the section travel across a white screen in which a single pin-prick had been made. A lamp behind the screen illuminated the pin-hole which served as a reference point. Section 1 of table 2 was measured in this way by Mr Mills, who made three traverses and obtained the average result of 41 per cent, which is in close agreement with that obtained with the photometer. A single traverse by another observer gave 42.1 per cent. This again supports the value obtained with the photometer.

(iv) *Summary of comparative tests.* Table 5 summarizes the average results obtained by means of the various methods tried.

This seems to show conclusively that the error lies in the use of the Shand's micrometer for microscopic observation. The most probable explanation seems to be that, since the eye-piece pointer is dark in tone and has finite, though small,

* This process is exceedingly tedious and I am indebted to Mr Mills, of the Section of Wood Structure in the Laboratory, for this painstaking work, as also for the measurements made on the Shand's micrometer.

Table 5. Comparison of results for cell-space ratio by different methods

Method	Cell-space ratio				
	Ash (section 1)	Scots pine (section 11)	Sycamore	Paper grid 1 (green)	Paper grid 2 (red)
Shand's micrometer	54	52	44	—	—
Photometer	41.5	41.8	31	48.5	50.7
Projection with Shand's method	41	—	—	—	—
Projection on squared paper	—	39	30.7	—	—
Travelling microscope	—	—	—	49.6	50.9

width, there is a tendency to make this pointer overlap on the *dark* side of the dividing line between cell space and cell wall. This in the extreme case would introduce an error equal to the pointer-width in each cell measured, and this over a large number of small cells will amount to an appreciable figure, giving an excess value to the cell spaces.

§ 7. CONCLUSIONS

The apparatus described above has been used successfully in this Laboratory. If we leave out of account the time required for the sodium light and the amplifier to settle down after switching-on, the time required for the actual measurements on 12 sections is approximately as follows:

Selection of matching filters	60 min.
Measurement of Q_2/Q_0 and Q_1/Q_0	40 min.
Total	1 hr. 40 min.

The time required to measure a section by taking three traverses with the Shand's micrometer is about 20 minutes, so that the time for the twelve sections is 4 hours. The time needed for mounting the sections and computing the results is the same by either method.

§ 8. ACKNOWLEDGMENTS

My thanks are due to members of the staff of the Section of Wood Structure in this Laboratory for their valuable cooperation in this work, and to the Director of the Forest Products Research Laboratory, Mr W. A. Robertson, for permission to publish the paper.

APPENDIX: AMPLIFIER USED IN THE PHOTOELECTRIC MEASUREMENT OF CELL-SPACE RATIO

The photoelectric current from the photocell is amplified and measured by a null method which is a modification of that described by Campbell and Ritchie*. The circuit is shown in figure 4.

* *Photoelectric Cells*, p. 141 (Pitman, 1930).

The bridge, consisting of valves 1 and 2 (chosen with steep characteristics) together with resistances R_1 and R_2 , can be balanced by adjusting R_{1A} , with R_{1B} as fine adjustment, together with the potentiometer P_3 , which alters the ratio of the filament currents in the two valves. If the cell P is dark and the potentiometers P_{2A} and P_{2B} are at zero, each valve has the same grid-bias through $E_g 1$. Under these conditions the bridge is taken through a series of balances until a small change in the main filament current, made by short-circuiting the resistance r_1 , produces no change in zero of the galvanometer. If the cell is now illuminated, the bias on V_1 becomes less negative owing to conduction through P , but may be restored to its former value by tapping off the necessary extra potential from $E_g 2$ and thus rebalancing the bridge. This extra potential is measured and is proportional to the intensity of the light falling on P_1 , no calibration of the valves being necessary.

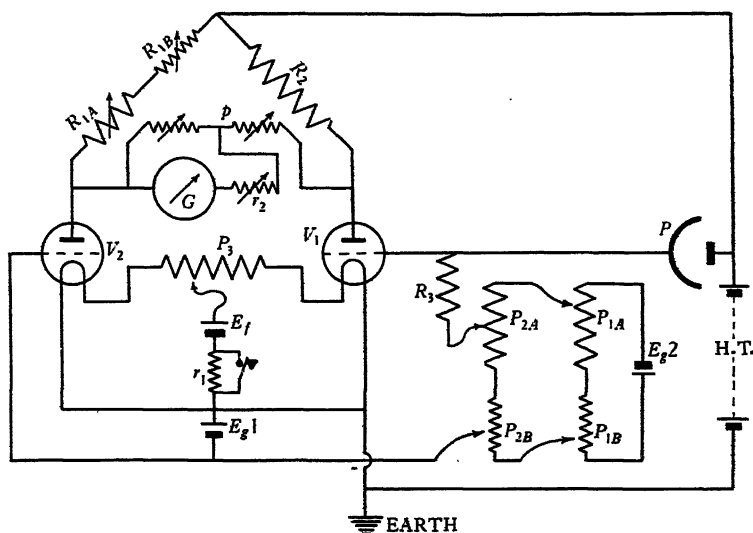


Figure 4. Photoelectric amplifier circuit. P , caesium coated vacuum cell giving saturation below 120 V.; V_1 and V_2 , Mullard. P.M. 1.H.L. 2-150 V.; r_1 , 1 Ω ; R_{1A} and P_{1A} , 20,000 Ω ; R_2 , 15,000 Ω ; R_{1B} and P_{1B} , 400 Ω ; R_3 , 2 to 8 M Ω . according to sensitivity required; P_{2A} , 100 steps of 200 Ω ; P_{2B} , 200 Ω . (dial marked in 20- Ω . steps); P_3 , 4 Ω ; $E_g 1$, 1.5-V. dry battery; $E_g 2$ and E_f , 2-V. accumulators; H.T., 120 V.

P_{2A} is a 100-stud potentiometer having steps of 200 Ω , specially made by Messrs Gambrell Bros. P_{2B} is a slide-wire potentiometer with a total resistance of 200 Ω . P_{2A} , with P_{2B} for steps of less than 1 per cent, records directly the intensity of any light as a percentage of a brighter one* and is used as follows: After the dark balance has been obtained P_{2A} is put at 100 per cent and P_{2B} at zero, the cell is fully illuminated through the clear portion of the microscope slide, and the balance of the bridge is restored by P_{1A} , with P_{1B} as fine adjustment, giving $Q_0 = 100$ per cent. P_1 is now kept constant, and any other, smaller, intensity

* Strictly speaking part of P_{2A} is shunted by the current through the grid-leak R_3 and the photocell P , but as this current is extremely small even at full illumination it may be disregarded, and equal increments of P_{2A} may be taken as equal increments of the potential on the grid of the valve V_1 .

Q_1 or Q_2 may be compared with the first by balancing with P_{2A} only, and P_{2B} for steps of less than 1 per cent. This device saves much calculation and gives directly the value of the ratio required. Moreover, changes in the intensity of the source are at once noticed, since the setting of P_1 for 100-per-cent illumination is independent, in relation to the dark zero, of changes in the rest of the circuit.

Frequent checking of the dark setting is necessary to correct a tendency to slow drift of zero. This drift is in part caused by any local temperature-changes and may be reduced by lagging the casing of the amplifier.

The sensitivity of the galvanometer may be adjusted to suit any maximum intensity of light by means of a potentiometer and series resistance, p and r_2 , figure 4, and is set to give the most rapid dead-beat swing with a deflection of about 5 mm. to 10 mm. for a 1-per-cent change in light*. The amplifier is enclosed in a light-tight earthed metal case. As an extra precaution against stray light the photocell is also cased in black paper which is in contact with the cell only at the base.

DISCUSSION

Lord RAYLEIGH said that in measuring the area of the holes in wire gauze he had obtained by far the most convincing results by means of a photoelectric cell. Photometric measurements used to be regarded as the most difficult of all, but modern equipment had brought such measurements within the domain of electrical measurement, and electrical measurements are in general easier to carry out than any other.

Mr J. E. CALTHROP enquired whether the method was applicable to small particles, such as lycopodium powder with a diameter of about 0.03 mm., or would diffraction vitiate the results?

Mr J. GUILD suggested that the transmitted light might be collected in an integrating sphere in order that errors due to diffraction might be eliminated.

Mr T. SMITH. The author has established a method for the examination of wood which he finds to be at once more rapid and more accurate than those used previously. The only surprising feature is that with so large a number of small cells the author has found no sign of diffraction. The answer to the question concerning the mutual effect of the cells on diffraction is that each aperture diffracts as if the others were absent, but the size and arrangement of the cells as a whole affect the distribution of the diffracted light in space.

Dr E. G. RICHARDSON. I should like to ask whether the apparatus would be suitable for a ready determination of the suitability of a given specimen of wood to support a load under unfavourable conditions, such as wet surroundings? I am thinking particularly of the testing of wood for use as pit props. With regard to the

* In cases where a brighter light-source can be used, the galvanometer may with advantage be replaced by a dial-pattern centre-zero microammeter (e.g. Gambrell's) which greatly increases the speed at which measurements can be made.

difficulty of instituting a comparison test of the method, to which the author refers, he might have examined the light passing through a suspension of sand in water vigorously stirred in a glass tank. It has been shown both theoretically and by pipette sampling that with complete turbulence the sand is distributed in the water exponentially with respect to height*. Such a suspension is, of course, the obverse of the author's microsections, but I have found that the light transmitted through such a system at different heights, with reference to clear water as standard, is proportional to the theoretical distribution as long as the concentration is not too high; and this would seem to indicate if the two experiments are comparable that the author may allay his fears with regard to scattered light upsetting the results. The trouble with regard to change of intensity of source during an experiment may be obviated by using two well-matched cells in a sort of photoelectric Wheatstone's Bridge.

AUTHOR'S reply. If the transmitted light were measured by means of an integrating sphere, light scattered from the translucent cell wall would be picked up as well as that from the holes and would have to be allowed for in the choice of matching filter. This could not be done unless the filter were of material identical, except for the holes, with that of the section, which is hardly practicable. In the present form of the apparatus this cell-wall scattering is allowed for, since the matching filter is chosen in respect of the light transmitted normally, and whether the rest of the light is scattered or absorbed is of no importance.

I am comforted by Dr Richardson's experiments showing that the scattered light does not upset his results. I think the reason is that the area of the suspension (or, in my case, of the section) which is illuminated is considerably larger than the area under test whose image falls on the aperture of the photocell. Thus as much light will be scattered on to the aperture from the surrounding suspension as away from it by the area under examination. Provided that the scattered light is roughly the same from all parts of the suspension, this will give an automatic compensation for scattering up to considerable angles from the normal.

Owing to the small amount of use to which this apparatus has so far been put, it is premature to say how far it would assist Dr Richardson in his problems of pit props, but from other work on pit props which has been done in this Laboratory† it would seem that the cell-space ratio within the timber is not by any means the only factor determining its suitability for pit props.

* Hurst, *Proc. R.S.* 124, 196 (1929).

† "Home-grown pit props," *F.P.R.L. Bulletin* No. 9 (1931).

THE MID-COURSE METHOD OF FITTING A PARABOLIC FORMULA OF ANY ORDER TO A SET OF OBSERVATIONS

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ABSTRACT. A meaning for the closeness of fit of a formula which is considered widely applicable in physics is suggested, and a method of deriving the most closely fitting parabolic formula of a given order is described. Geometrically the formula represents the mid course between the most outlying points.

§ 1. PRINCIPLES OF THE METHOD

IT is no rare occurrence in physics for the problem of fitting a formula of the type

$$y = a + bx + cx^2 + \dots + kx^{n-1},$$

where corresponding values of x and y are given, to arise, and a number of papers have been written on the procedure to be followed. These show that there is considerable diversity of opinion on the way in which the problem should be solved. Some methods, for instance graphical methods, are advocated because of the simplicity of the numerical work involved, and others, for example the method of least squares, because they are claimed to lead to the most accurate results. But even when accuracy is admittedly of outstanding importance, different methods, leading to somewhat different results, are advocated by different writers. I suggest that the reason for this disagreement is to be found in the absence of any clear statement of what is to be understood by accuracy. There is no single criterion of accuracy or closeness of fit which is of general applicability. It will, I think, be generally conceded that there are problems in which a stationary value of $\Sigma (\Delta y)^2$ is the criterion which ought to be applied. In others this sum may perhaps require to be replaced by $\Sigma \{A (\Delta x)^2 + 2B \Delta x \Delta y + C (\Delta y)^2\}$, where A , B , C are constants which depend upon factors special to the particular problem and upon the scales on which x and y are measured. But in many physical problems no variant of the method of least squares is of special interest as a means of constructing a formula of the type we are considering. The more usual requirement is that for any value of x in a given range the formula should give y correct within certain fixed limits. If y is required to be correct to three significant figures, to point out that the formula is almost everywhere correct to four or five figures is no answer to the objection that in one or two places it is wrong in the second figure. Since this is the type of error-compensation to which the least-squares method may lead, we clearly ought only

to employ this method when an examination of the problem shows that a solution of this kind is required. In physics the value of a formula depends much more frequently on the size of the maximum error to which its use can lead.

The relative values of empirical formulae of the polynomial type may be measured roughly by the inverse of the number of terms they contain. For this reason we almost always employ a shorter expression than the one which would represent the observations exactly. The formula then in general yields values of y differing by smaller or larger amounts from the actual experimental results. The problem to be considered here is the determination of the coefficients a, b, c, \dots so that none of the larger discrepancies exceed a minimum value; the smaller discrepancies will not trouble us. In other words, we completely neglect all the observations that fall in mean positions and determine our coefficients from the outlying observations alone. If the extreme errors prove to be too great the order of the polynomial must be increased. The outlying observations can usually be selected without difficulty by plotting y against x , but it may sometimes be necessary to plot $y - \phi(x)$ against x , where $\phi(x)$ is an approximate expression for y . The number of outlying points should be one more than the number of terms in the polynomial, and therefore two more than the order of the polynomial. As x increases from its lowest to its highest value they must be chosen to lie alternately on opposite sides of the mean locus of points.

Assume for the moment that we can find values for the n coefficients so that

$$f(x) \equiv a + bx + cx^2 + \dots + kx^{n-1}$$

yields values of y for the outstanding observations which are all in error by the same amount but alternately of opposite signs. Thus if $x_1, x_2, x_3, \dots, x_{n+1}$ are the values of the independent variable for the selected observations, arranged as an ascending or as a descending sequence, we have

$$y_1 - f(x_1) = f(x_2) - y_2 = y_3 - f(x_3) = f(x_4) - y_4 = \dots = \epsilon.$$

Then $f(x)$ is in error by $-\epsilon$ at x_1, x_3, x_5, \dots , and by $+\epsilon$ at x_2, x_4, x_6, \dots , and by amounts not exceeding these limits at all the other observed points.

By an argument which has been given before* in a somewhat different problem but which may be worth repeating here, it can be shown that $f(x)$ is the polynomial of order $n - 1$ which fits the observations best. If possible suppose that $g(x)$ is a polynomial of order not greater than $n - 1$ which represents y with errors not exceeding the narrower limits $\pm |\eta|$. Then if ϵ is positive

$$f(x) - g(x) < -\epsilon + |\eta| < 0 \text{ for } x = x_1, x_3, x_5, \dots$$

and
$$f(x) - g(x) > \epsilon - |\eta| > 0 \text{ for } x = x_2, x_4, x_6, \dots$$

If ϵ is negative the same results hold with the interchange of the sets x_1, x_3, x_5, \dots and x_2, x_4, x_6, \dots . In either event it follows that the polynomial $f(x) - g(x)$, which at most is of order $n - 1$, vanishes for at least n different values of x in the interval x_1 to x_{n+1} . But this is only possible if $f(x)$ and $g(x)$ are identically equal, and this is inconsistent with the supposition that $|\eta|$ is less than $|\epsilon|$. The poly-

* *Proc. Phys. Soc.* 33, 141 (1919-20).

nomial $f(x)$ is therefore the one which yields the least extreme errors in y , and is therefore the expression desired.

The actual construction of the polynomial is very simple. Let

$F(y_1, y_2, y_3, y_4, \dots)$, standing for

$$\sum_{r=1}^{n+1} \frac{y_r (x - x_1)(x - x_2) \dots (x - x_{r-1})(x - x_{r+1}) \dots (x - x_{n+1})}{(x_r - x_1)(x_r - x_2) \dots (x_r - x_{r-1})(x_r - x_{r+1}) \dots (x_r - x_{n+1})},$$

be the Lagrangian polynomial of order n which passes through the $n + 1$ given points. Then, if x_1, x_2, x_3, \dots are regarded as fixed, $F(1, -1, 1, -1, \dots)$ is a polynomial of order n which yields the values $1, -1, 1, -1, \dots$ at $x_1, x_2, x_3, x_4, \dots$. Let the coefficient of x^n in $F(y_1, y_2, y_3, y_4, \dots)$ be ϵ times the coefficient of x^n in $F(1, -1, 1, -1, \dots)$. Then

$$f(x) = F(y_1, y_2, y_3, \dots) - \epsilon F(1, -1, 1, -1, \dots)$$

is a polynomial, of order $n - 1$ at most, which assumes the values

$$y_1 - \epsilon, y_3 - \epsilon, y_5 - \epsilon, \dots \text{ at } x = x_1, x_3, x_5, \dots$$

and the values

$$y_2 + \epsilon, y_4 + \epsilon, y_6 + \epsilon, \dots \text{ at } x = x_2, x_4, x_6, \dots$$

That is to say $f(x)$ is the expression required, and ϵ is the magnitude of the extreme error. It may be observed that though $F(y_1, y_2, y_3, \dots)$ is of higher order than $f(x)$ it is liable to yield errors amounting to about 2ϵ , i.e. twice as great as those possible with $f(x)$.

If it is preferred we can write down explicit formulae for ϵ, a, b, c, \dots . Let $(r)_p$ denote the sum of the homogeneous products of the x 's taken p at a time, x_r being excluded. Denote

$$\sum_{r=1}^{n+1} \frac{y_r (r)_p}{(x_1 - x_r)(x_2 - x_r) \dots (x_{n+1} - x_r)} \text{ by } Y_p$$

and

$$\sum_{r=1}^{n+1} \frac{(-1)^r (r)_p}{(x_1 - x_r)(x_2 - x_r) \dots (x_{n+1} - x_r)} \text{ by } X_p,$$

where the denominators represent the continued product of the excess of all the other x 's over x_r . Then if the sign of ϵ is unchanged from the preceding expressions the formulae required are

$$\begin{aligned} -\epsilon &= Y_0/X_0, \\ a &= Y_n + \epsilon X_n, \\ -b &= Y_{n-1} + \epsilon X_{n-1}, \\ c &= Y_{n-2} + \epsilon X_{n-2}, \\ -d &= Y_{n-3} + \epsilon X_{n-3}, \end{aligned}$$

and so on. The first of these equations may be used to determine whether the $n + 1$ observations have been chosen correctly. The choice is correct if the substitution of any other observations for one or more of those selected yields a smaller absolute value of ϵ .

If formulae cast into a particular mould are desired it is best to start from these

equations. As an example the divided-difference formulae for fitting an ordinary parabola are

$$c = \frac{\frac{y_1 - y_3}{x_1 - x_3} - \frac{y_2 - y_4}{x_2 - x_4}}{x_1 - x_2 + x_3 - x_4},$$

$$b = -\frac{\frac{y_1 - y_3}{x_1 - x_3}(x_2 + x_4) - \frac{y_2 - y_4}{x_2 - x_4}(x_1 + x_3)}{x_1 - x_2 + x_3 - x_4},$$

$$a + \epsilon = \eta_{13} + cx_1x_3, \quad a - \epsilon = \eta_{24} + cx_2x_4,$$

where η_{13} , η_{24} are the ordinates of the points in which the chords 1, 3 and 2, 4 meet the y axis, so that

$$\eta_{13} = \frac{x_1y_3 - x_3y_1}{x_1 - x_3} = \frac{y_1 + y_3}{2} - \frac{y_1 - y_3}{x_1 - x_3} \cdot \frac{x_1 + x_3}{2},$$

$$\eta_{24} = \frac{x_2y_4 - x_4y_2}{x_2 - x_4} = \frac{y_2 + y_4}{2} - \frac{y_2 - y_4}{x_2 - x_4} \cdot \frac{x_2 + x_4}{2}.$$

For a cubic the simplest formula is perhaps

$$f(x) + \epsilon = y_1 \frac{(x - x_3)(x - x_5)}{(x_1 - x_3)(x_1 - x_5)} + y_3 \frac{(x - x_1)(x - x_5)}{(x_3 - x_1)(x_3 - x_5)} + y_5 \frac{(x - x_1)(x - x_3)}{(x_5 - x_1)(x_5 - x_3)} \\ + \frac{2(x - x_1)(x - x_3)(x - x_5)}{x_1^2 - x_2^2 + x_3^2 - x_4^2 + x_5^2 - (x_1 - x_2 + x_3 - x_4 + x_5)^2} \left[\frac{(y_1 - y_3)(x_2 - x_3 + x_4 - x_5)}{(x_1 - x_3)(x_1 - x_5)} \right. \\ \left. - \frac{y_2 - y_4}{x_2 - x_4} + \frac{(y_3 - y_5)(x_1 - x_2 + x_3 - x_4)}{(x_5 - x_1)(x_5 - x_3)} \right].$$

The full equation for ϵ is

$$\{x_1^2 - x_2^2 + x_3^2 - x_4^2 + x_5^2 - (x_1 - x_2 + x_3 - x_4 + x_5)^2\} \epsilon \\ = \frac{y_1(x_2 - x_3)(x_2 - x_5)(x_3 - x_4)(x_4 - x_5)}{(x_1 - x_3)(x_1 - x_5)} - \frac{y_2(x_1 - x_4)(x_3 - x_4)(x_4 - x_5)}{(x_2 - x_4)} \\ + \frac{y_3(x_1 - x_2)(x_2 - x_5)(x_1 - x_4)(x_4 - x_5)}{(x_1 - x_3)(x_3 - x_5)} - \frac{y_4(x_1 - x_2)(x_3 - x_3)(x_2 - x_5)}{(x_2 - x_4)} \\ + \frac{y_5(x_1 - x_2)(x_1 - x_4)(x_2 - x_3)(x_3 - x_4)}{(x_1 - x_5)(x_3 - x_5)},$$

but usually it will be more easily obtainable by substituting x_3 or x_4 for x after the numerical expression for $f(x) + \epsilon$ has been found, and using

$$\epsilon = f(x_2) - y_2 = f(x_4) - y_4.$$

As the order of the curve increases it becomes less profitable to construct special algebraic formulae. The least amount of computation will probably then follow from the restriction of the homogeneous sums to the case when all the points are included. This is accomplished by writing the polynomial formally as the product

$$(x - x_1)(x - x_2) \dots (x - x_{n+1})(x^{-2}A_1 + x^{-3}A_2 + x^{-4}A_3 + \dots),$$

it being understood that in the final product negative powers of x are to be omitted. The A 's (including two additional quantities A_0 and A_{-1}) are then found from

$$A_p = \Sigma \frac{y_r x_r^p}{\pi_r} + \epsilon \Sigma \frac{(-1)^r x_r^p}{\pi_r},$$

where

$$\pi_r = (x_r - x_1)(x_r - x_2) \dots (x_r - x_{n+1})$$

and ϵ is given by $A_0 = 0$. The constant term can also be evaluated directly as $x_1 x_2 \dots x_{n+1} A_{-1}$. The calculations can be checked in the course of the work from the identities

$$\Sigma \frac{x_r^p}{\pi_r} = 0 \quad (p = 0, 1, 2, \dots, n-1),$$

$$\Sigma \frac{1}{x_r \pi_r} = \frac{(-1)^n}{x_1 x_2 \dots x_{n+1}}, \quad \Sigma \frac{x_r^n}{\pi_r} = 1,$$

which are also useful in reducing the labour involved in constructing special formulae such as those already given for the cubic case.

§ 2. NUMERICAL EXAMPLES

It is of interest to see how results obtained by this mid-course method compare with those given by other methods. We take first of all a simple example given by Merriman. The abscissae and ordinates of four points on a straight line were measured with equal precision, giving

$$y = 0.5, 0.8, 1.0, \text{ and } 1.2,$$

$$x = 0.4, 0.6, 0.8, \text{ and } 0.9.$$

By considering errors in x and y simultaneously Merriman reaches the least-squares solution

$$y = 1.348x - 0.035.$$

From a graph it is easily seen that the first point lies closer to any reasonable mean line than the other three. The slope of the mid-course line is thus determined from the second and fourth points and is $(1.2 - 0.8)/(0.9 - 0.6)$ or $4/3$, and it at once follows that the line given by the method of this paper is

$$y = (40x - 1)/30.$$

For the given values of x the errors in y by the two methods are

Least squares	0.0042,	- 0.0262,	0.0434,	- 0.0218.
Mid course	0.0000,	- 0.0333,	0.0333,	- 0.0333.

If the points and these lines are plotted it is not possible from the graph to say that one is a better fit than the other. The squares of the errors sum to 0.00306 and 0.00333 respectively, so that even from the least-squares point of view the solution we have found with such little trouble cannot be substantially improved.

If we did not know that the points were supposed to be on a straight line we might consider whether a parabola would give a better fit. The reduced formulae give

$$c = \frac{10}{33}, \quad b = \frac{11}{12}, \quad a \pm \epsilon = c \times 0.32, \quad a \mp \epsilon = c \times 0.54$$

or $\epsilon = 0.0305$. The reduction in the error is therefore trivial, and there is no justification for preferring a parabola to a straight line.

The next example from Merriman has been utilized by Awbery. The temperatures encountered at different depths in boring a deep Artesian well were found to be

Depth x (m.)	28	66	173	248	298	400	505	548
Temperature y ($^{\circ}\text{C.}$)	11.71	12.90	16.40	20.00	22.20	23.75	26.45	27.70

From a graph the first, third, fifth and sixth points were selected. The mid-course solution found for an ordinary parabolic formula is

$$y = 9.694 + 0.047395x - 0.000026206x^2.$$

Awbery obtained by the zero-sum method

$$y = 9.745 + 0.049495x - 0.0000322x^2,$$

and I find for the least-squares solution

$$y = 10.214 + 0.044227x - 0.000023115x^2.$$

(Merriman's solution, $y = 10.6 + 0.0415x - 0.0000193x^2$, is subject to the condition $y = 10.6$ when $x = 0$.)

The errors due to the use of these formulae are given in table 1.

Table 1

x	Mid course	Zero sum	Least squares
28	- 0.71	- 0.60	- 0.28
66	- 0.19	- 0.03	+ 0.13
173	+ 0.71	+ 0.94	+ 0.77
248	- 0.16	+ 0.04	- 0.24
298	- 0.71	- 0.56	- 0.86
400	+ 0.71	+ 0.64	+ 0.46
505	+ 0.50	+ 0.08	+ 0.20
548	+ 0.10	- 0.50	- 0.19

From these figures it is apparent that the zero-sum curve, which almost passes through the second, fourth and seventh points, is nearer the least-squares solution than the mid-course solution, though the parabolas for the latter two agree much more closely in the position of the axis and the length of the latus rectum than either of them do with the zero-sum solution.

As a final example from Merriman we take one in which the accuracy of fit by a parabolic formula corresponds more closely to accurate physical measurements. The data give the velocities v of the water of the Mississippi at different depths d : they, and the outstanding errors with the mid-course and least-squares solutions, are given in table 2.

Under these conditions there is little to choose between the solutions, and the chief advantage of the mid-course method is the relatively small amount of labour involved in reaching an acceptable solution.

The problem we have been considering is essentially that known to the statis-

Table 2

d	v	Mid course	Least squares
0.0	3.1950	+ 0.0027	+ 0.0001
0.1	3.2299	+ 0.0036	+ 0.0018
0.2	3.2532	+ 0.0009	- 0.0002
0.3	3.2611	- 0.0016	- 0.0021
0.4	3.2516	- 0.0020	- 0.0019
0.5	3.2282	- 0.0036	- 0.0031
0.6	3.1807	+ 0.0036	+ 0.0044
0.7	3.1266	+ 0.0022	+ 0.0033
0.8	3.0594	- 0.0012	0.0000
0.9	2.9759	- 0.0036	- 0.0024

tician as "smoothing," with the restriction that the smooth curve is to be represented by a simple algebraic formula. It becomes of interest to consider how the results obtained by the method of this paper compare with those reached by approved

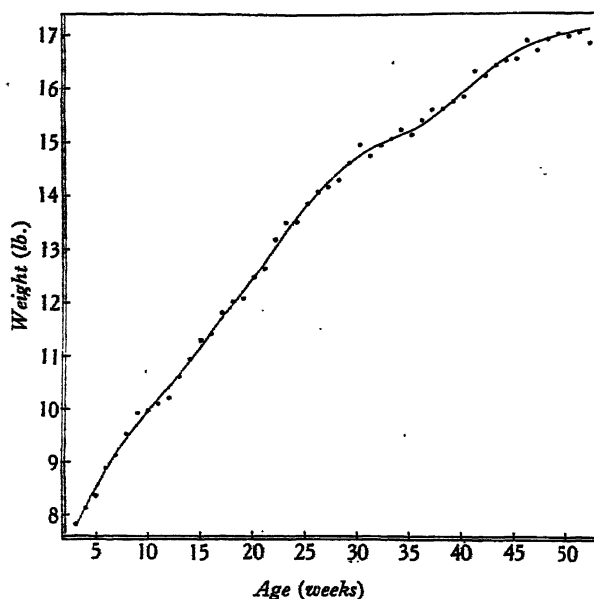


Figure 1. Weight of babies plotted against age, with Rhodes's smoothed values shown as a continuous curve.

methods of smoothing. For this purpose I have taken two of the examples given by Rhodes* in his tract on smoothing. The first of these represents the weight of babies according to age for their first year. The observations and Rhodes's smoothing are shown in figure 1. Actual values are not however quoted for the first seven and the last six points plotted, so that I have been forced to consider only the central three-quarters of the plot. The points shown ringed in figure 2 were chosen by eye as likely to be the most outstanding, and as they were four in

* *Tracts for Computers*, No. 6 (Cambridge University Press).

number an ordinary parabola was fitted. The curve is seen to be a good general fit and it happens to fit equally well over the whole range of the points shown in figure 1. The question now arises whether the departures of the points from the curve ought to be treated as accidental or not. If the measurements referred to a normal physical problem I should consider any attempt to improve upon this result as unjustified. We can do a little to bring the curve nearer the majority of the points by adding the first point to the other four and fitting a cubic, but the improvement is so small that it is doubtful whether it is worth making. If the undulations in the curve of figure 1 have a meaning, figure 2 illustrates a stage beyond which the mid-course method as it has been developed here is inapplicable.

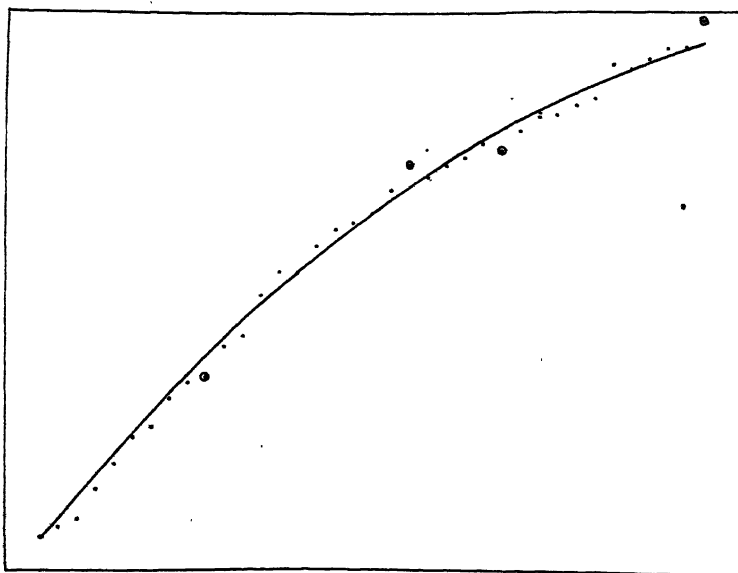


Figure 2. The mid-course parabola fitted to the points of figure 1.

Figure 3 is an example where the scatter of the points is considerable. The points represent variation of mortality with age, and their distribution suggests a cubic curve to the eye. It is easy to pick out five points likely to represent extreme departures from the curve: they are distinguished in the figure by large circles. The cubic curve based on these points extends from near the top left-hand corner to the bottom right-hand corner. Though the curve agrees very fairly with the run of the points, it is apparent that considerable improvement is possible in the right half of the diagram but that the points on the left are too scattered to leave correspondingly small residuals. By adding the two points marked with smaller circles we push the curve further away from these two points, while bringing it nearer to the five points originally selected. The new quintic curve is shown by a second full line, and, with the exception of the first third, represents the data very satisfactorily. The smoothing may be extended without difficulty—say by means of a cubic curve

—into the remaining part of the diagram with extreme errors somewhat less than those obtained with the original cubic. No substantial improvement on this result is likely to be obtainable, and we may infer from this and the preceding example

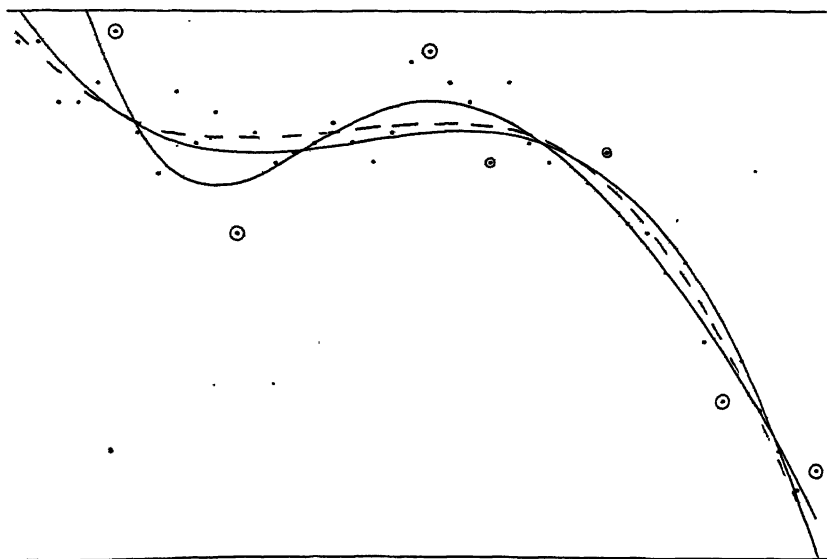


Figure 3. The full lines represent the mid-course cubic and quintic; the broken line represents the least-squares cubic.

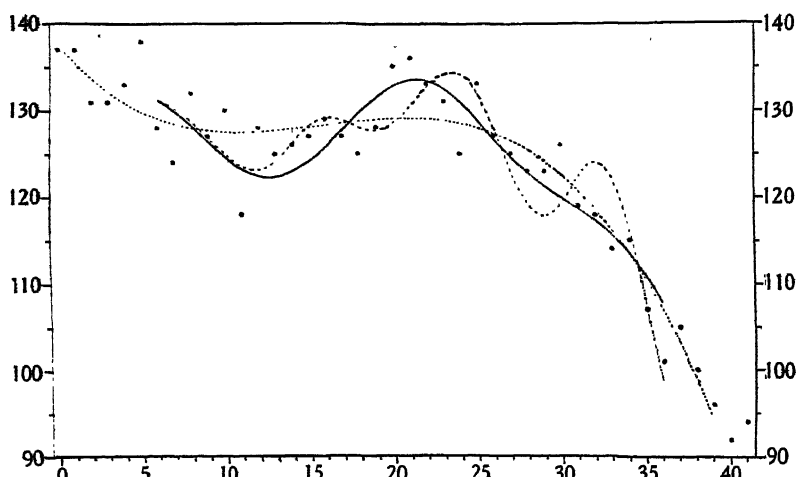


Figure 4. Smoothing of mortality curve. cubic; ——— osculatory method A; ----- osculatory method B; original data.

that the mid-course method is not unlikely to be applicable in some statistical problems where it may well be held that the method of least squares has clearer justification than in some branches of physics.

The broken curve of figure 3 represents approximately the cubic curve obtained by the method of least squares. This curve is shown accurately in figure 4, which is taken from Rhodes's pamphlet*, where the results of smoothing in the central region by two other methods are shown. From one of the examples it is clear that smoothing can be carried out in ways which lead to mere misrepresentation of the significant features of the data. This is not possible with the mid-course method if it is used intelligently. The other curve is free from faults of this kind, but it certainly does not represent the observations better than the curves obtained here, though its derivation involves much more labour.

§ 3. ACKNOWLEDGMENT

I have to thank the Director of the Department of Applied Statistics, University College, London, for permission to reproduce figures 1 and 4 from Rhodes's tract, to which reference has already been made.

DISCUSSION

Lord RAYLEIGH said that the paper perhaps hardly took sufficient account of the difference between an error and a mistake. Suppose that fifty observations had the value $A + dA$ and one the value $A - dA$. According to the author the best value would be A , but this conclusion would hardly appeal to a betting man, and still less would it do so if the fifty-one observations were made by fifty-one different observers. In the case of heterochromatic photometry some observers were very confident while others were positively tortured by doubt when making a setting. Probably there was that element of doubt, to a greater or less extent, in all observations. The main use of methods of reducing observations by least squares and the like was to enable a man to state his results succinctly without faking them. It might be doubted whether such methods had ever produced real knowledge in the shape of a discovery unless perhaps in proving the reality of stellar parallax. The speaker had been taught in his youth that the theory of errors of observation was a thing to be learned and then forgotten. But at all events such methods as that of the author would save weary hours of arithmetic.

Mr J. H. AWBERY. Mr Smith has put forward a criterion for accuracy of fit which has much to recommend it, and merits careful consideration. There will doubtless be many cases—the derivation of a formula to represent the observed (mass, luminosity) relation in stars is perhaps one—where it is the best criterion, but I do not think it will often be suitable in pure physics. Take for example the extreme case of a formula of degree zero in the independent variable in which we have a number of estimates of a single quantity. Mr Smith's method would take as a representative value the mid-point between the greatest and least of the estimates. If these are measurements of a physical quantity, my objections to this

* In the original diagram about one-quarter of the points are incorrectly plotted. These errors have been corrected in this diagram.

are (1) that a single further repetition which gives a bad result can alter the representative value, and (2) that no account is taken of the possibility of mistakes, as distinct from errors. That Mr Smith sees the matter differently is clear, when he speaks of the case where a formula is almost everywhere accurate to four or five figures, but is wrong in the second figure at a few points. I agree with him, that the formula is condemned, if the observations are indisputable; but if they were measurements of a pair of physical variables, I should draw the conclusion that observations ought to be repeated at the points where the large discrepancies occur.

It is clear that the selection of the best criterion depends on the nature of the problem; it is probably also in some degree a matter of taste, depending on one's psychological make-up. However that may be, we must be grateful to Mr Smith for his very skilful formulation of the method to be followed in deriving the formula, on those occasions when it has been decided that his criterion is to be adopted.

MR T. W. ADAMS. Would Mr Smith say what he regards as the limitations of his method of computation? Does he regard the method as applicable to physiological and biological data, i.e. to vital statistics?

MR J. GUILD. I think that the difficulty which some participants in the discussion find in accepting the mid-point criterion put forward by Mr Smith is partly due to a failure to distinguish between two quite different types of case. Suppose we have a set of values for x and y , and that the values of y depart irregularly from a parabolic or other simple function of x , and that it is our intention to find the constants of such a function which best represents the relation. Two distinct cases may arise. In one case the given values of x and y may be exact, or at any rate only subject to errors of measurement which are negligible compared to the departures of the individual y 's from the corresponding values of $f(x)$. In other words, the data accurately represent the facts, which do not actually fit any simple formula of the proposed type. We may nevertheless, for various reasons, desire to find, say, a parabolic formula which *most nearly* fits the facts. Our problem is to find the constants in an admittedly approximate relation which will depart from the truth by the smallest practicable amount at any value of x taken at random. In such a case any of the given values of y is as important as any other and the criterion adopted by Mr Smith is clearly the only logical one to apply. The other type of case, which is of much greater importance to the experimental physicist, is when the departures of y from the corresponding values of any simple function of x are of the same order as the errors of observation, that is to say, when one or more functions can be found which represent the experimental data to within the accuracy of the observations. This case arises frequently in physical measurements, as for example, in determining the resistance-temperature relation of a resistor, the e.m.f.-temperature relation of a thermocouple, and so on.

The classical principles for the reduction of such observations treat this case as exactly equivalent to the former. It is assumed that every observation is of equal importance and must be weighted in accordance with a prescribed mathematical procedure—in brief, the method of least squares. I recall that when learning

physics in my school days, every figure, once it was recorded in the notebook, became sacrosanct: it must not be rubbed out, or amended, or one's reputation for honesty was seriously compromised. To use one's intelligence in discarding obviously anomalous results was regarded as "faking" the answer. This principle is still applied in the teaching of experimental science, and is based on the proposition that as every observation is made in ignorance of any predisposing cause of error (otherwise it wouldn't be made) there is no reason for considering one observation more or less reliable than another: the probability of being right is the same for all. This proposition is false. Probability always means, or should mean, probability in the light of the available evidence. At the moment when each observation is made, the probability of its being correct is the same as for any other of the series, but this is no longer the case when the whole series is completed and available for inspection. The trend of the observations, as a whole, constitutes additional evidence which affects the estimate of probability to be applied to any one observation. It provides logical justification for cutting out observations which are abnormal before proceeding to the formal reduction. As to what constitutes an abnormal observation there is no formal rule which can replace the intelligence of the experimenter: his criterion will be based on experience of the particular kind of measurement which is in question and accumulated knowledge of the behaviour of the apparatus; but a rough general rule, to be used with, not as a substitute for, intelligence is that any single observation which, if admitted, would appreciably alter the result from that obtained by leaving it out should be discarded. If too many of the observations turn out to be worthless when separately tested in this way we do not mend matters by leaving them in: the only remedy in such a case is to do the job over again with increased care or by improved methods. But every experimenter knows that even when all reasonable care has been taken anomalous observations tend to crop up. To reject these is not faking, but is merely the use of intelligence and a proper interpretation of probability, and any series of observations should have such outlying members pruned off before it is subjected to mathematical reduction. The experimenter who fails to do this, in deference to the classical misapplication of statistical theory to experimental observations, is merely permitting the intelligence which he has presumably brought to bear on the experimental part of the work to abdicate when he comes to the arithmetic.

A series of observations, cleaned of obvious errors, will never present the kind of anomalous distribution to which one would fear to apply Mr Smith's mid-course criterion.

I would submit, however, that in the case now being considered, where the irregularities to be smoothed out are of the same order as observational errors, there is no theoretical virtue in any particular method of finding the constants of the function, and that the only relevant consideration is the time involved in the computations. The difference in the function as evaluated by any reasonable methods represents the inherent ambiguity of the given data, and it is unjustifiable to assume that any one of the perfectly good curves which can be made to fit it is *true*er than another. One of the crimes to be laid at the door of the statisticians in their treat-

ment of experimental observations is that they have encouraged the belief that by suitable mathematical manipulation of irregular observations the true value of some quantity, or of the constants in some relation, can be established within limits of uncertainty which are in fact illusory. Ample proof of this is afforded by the literature: how often do we find different experimenters determining the same thing and disagreeing by amounts in excess of the sum of their estimated uncertainties as computed by the classical formulae. My experience is that any series of observations can be smoothed graphically with as much accuracy as the observations justify. Where mere smoothing is not enough and we want the constants of a functional relation, we cannot do better than employ whatever method gives these with the minimum amount of calculation. It seems clear, on the evidence, that the mid-course method is the best in this respect and that the least-squares method is far and away the worst.

AUTHOR'S reply. I have not attempted in the paper to deal with the observations, but have assumed that there is no reason to believe that any of them are mistakes and that the differences or scattering are such as are usually to be expected in the kind of experiment considered. Though under these conditions it would be very unusual to make as many as fifty measurements, yet circumstances can be imagined where the best value from fifty observations $A + dA$ and one $A - dA$ would be A . The point I would make is that the observer ought to consider the most important factors in each problem and not apply a stock method in a routine manner. I am interested to hear that Lord Rayleigh was advised to forget the theory of least squares, and I should like to see the same advice given generally to young physicists today.

In reply to Mr Adams: I should not hesitate to apply the mid-course method to any satisfactory set of quantities whenever I believed the result required was likely to lie in a central position between the extreme observations. I can imagine circumstances in which the method could reasonably be applied to vital statistics and kindred magnitudes.

I am in agreement with much that Mr Guild says, but I have not reduced the question of the rejection of observations to a definite set of rules in the way he has done. When there is no question of mistakes the problem seems to me to contain a number of difficulties. The fact that Mr Guild's work is regularly of very great accuracy may be considered a recommendation of the views he puts forward.

I agree with Mr Guild that many workers will find the small amount of arithmetic involved the most important property of the mid-course method. Its rapidity is of course due to the fact that only a few observations enter into the calculations. High-order curves are not often wanted, but I have recently compared various methods of computing the coefficients and have found the following general method particularly convenient. I assume that the polynomial to be obtained is of order $2n$, so that $2n + 2$ outstanding observations are utilized. Let the polynomial be

$$f(x) = a_1 x^{2n} + a_2 x^{2n-1} + a_3 x^{2n-2} + \dots + a_{2n+1}.$$

I find from the odd observations a linear matrix Y and square matrices S_q and R_q , each of order n . Their definitions are $Y = (Y_0, Y_1, Y_2, \dots, Y_{n-1})$,

$$S_q = \begin{pmatrix} s_q & s_{q+1} & s_{q+2} & \dots \\ s_{q-1} & s_q & s_{q+1} & \dots \\ s_{q-2} & s_{q-1} & s_q & \dots \\ \dots & \dots & \dots & \dots \end{pmatrix}, R_q = \begin{pmatrix} r_q & r_{q+1} & r_{q+2} & \dots \\ r_{q-1} & r_q & r_{q+1} & \dots \\ r_{q-2} & r_{q-1} & r_q & \dots \\ \dots & \dots & \dots & \dots \end{pmatrix},$$

where

$$(x - x_1)(x - x_3) \dots (x - x_{2n+1}) = x^{n+1} + s_1 x^n + s_2 x^{n-1} + \dots + s_{n+1} \\ = x^{n+1} \{1 + r_1 x^{-1} + r_2 x^{-2} + \dots\}^{-1},$$

$$Y_u = \sum_{v=0}^n \frac{y_{2v+1} x_{2v+1}^u}{(x_{2v+1} - x_1)(x_{2v+1} - x_3) \dots (x_{2v+1} - x_{2n+1})}.$$

From the even observations similar matrices Y', S'_q, R'_q are found. Then the first n of the coefficients a are given by

$$(a_1 a_2 a_3 \dots a_n) = (Y' S'_0 - Y S_0) (R_0 S_n - R'_0 S'_n)^{-1},$$

the succeeding n coefficients by

$$(a_{n+1} a_{n+2} \dots a_{2n}) = (a_1 a_2 \dots a_n) R_0 S_n + Y S_0 \\ = (a_1 a_2 \dots a_n) R'_0 S'_n + Y' S'_0,$$

and the constant term a_{2n+1} and the error ϵ by

$$y_u + y_v - 2a_{2n+1} = \{a_1 x_u^{2n} + a_2 x_u^{2n-1} + \dots + a_{2n} x_u\} + \{a_1 x_v^{2n} + a_2 x_v^{2n-1} + \dots + a_{2n} x_v\}, \\ y_u - y_v \pm 2\epsilon = \{a_1 x_u^{2n} + a_2 x_u^{2n-1} + \dots + a_{2n} x_u\} - \{a_1 x_v^{2n} + a_2 x_v^{2n-1} + \dots + a_{2n} x_v\},$$

where x_u, y_u and x_v, y_v are any two observations taken one from the even and the other from the odd set. Formulae for the polynomial of order $2n - 1$ may be derived by putting $x_{2n+2} = \infty$.

THE DETERMINATION OF A PARABOLIC FORMULA TO REPRESENT A SERIES OF OBSERVATIONS

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ABSTRACT. When the constants a , b and c in the formula $y = a + bx + cx^2$ are to be determined from simultaneous values of x and y , the best-known methods involve the addition of a number of equations, which are then solved to give the desired constants. A large number of significant figures must be retained in the calculation. It is pointed out that if one constant can be determined separately from the other two, the arithmetic can be greatly simplified. It is frequently of advantage to determine first the constant c , since this is the constant needed to correct mean values to instantaneous values. It can be easily found by the method of divided differences which, in contrast to the more familiar methods, reduces the number of significant figures to the minimum permissible. If the observations are very irregular, the method in its crudest form gives a very poor estimate of c , but a modification is described which adds little to the labour, whilst improving the accuracy very considerably.

Numerical examples are given, and the results by the new method compared with those obtained by the methods of least squares and zero sum.

§ 1. INTRODUCTION

THE parabolic equation $y = a + bx + cx^2$ is of common occurrence in physics and engineering, either as a rigorous equation, or as one to represent a series of results empirically. Its utility for the latter purpose has been stressed recently by various authors. For example, Tuttle and Satterly claim that in many cases it is preferable as an interpolation formula to the commonly adopted form $y = ax^n$.

When such a formula is to be adopted, a variety of methods are in use for determining the constants a , b and c from the observations. The authors just cited, for example, suggest drawing a curve to represent the observations, and, selecting three points from the curve, to provide three equations for a , b and c . Clearly this method is suitable only for relatively low accuracy. When greater precision is necessary, the two most familiar devices for obtaining three equations are the method of least squares and that of zero sum. The former involves a great deal of labour before the normal equations can be formed, whilst both methods demand the use of a considerable number of significant figures in the calculations, in order to obtain even a moderate number in the values of a , b and c .

To illustrate this, we may work a very simple example by the method of zero sum. It is desired to calculate a , b and c in the equation $y = a + bx + cx^2$ when the following values are given:

$x = 1$	2	3.5	4	5	8
$y = 1$	2	4	7	14	22

The first step is to write out the six quadratic equations, and to reduce them to three by adding in pairs. The result is

$$\left. \begin{aligned} 3 &= 2a + 3b + 5c \\ 11 &= 2a + 7.5b + 28.25c \\ 36 &= 2a + 13b + 89c \end{aligned} \right\} \dots\dots(1).$$

Subtracting each of these from the following one eliminates a and yields

$$\left. \begin{aligned} 8 &= 4.5b + 23.25c \\ 25 &= 5.5b + 60.75c \end{aligned} \right\} \dots\dots(2).$$

If, now, each of these is divided by the coefficient of (b) , with only slide-rule accuracy, they become respectively

$$\left. \begin{aligned} 1.775 &= b + 5.17c \\ 4.545 &= b + 11.03c \end{aligned} \right\} \dots\dots(3),$$

whence by subtraction

$$2.770 = 5.86c \dots\dots(4),$$

or

$$c = 0.473.$$

With this value in (3), $b = -0.67$; and then from (1) $2a = 2.64$ or $a = 1.32$.

The above approximate solution was carried out with a slide-rule, and it is now possible to estimate the accuracy really required. Since y is given only to the nearest integer, it is desirable that the formula should give the first decimal place. Now, when y is being calculated for $x = 8$, the contributions of the three terms are approximately 1.3, -5.3 and $+30.3$, and a should therefore be known to 2, b to 2 and c to 3 significant figures. Thus as regards c , equation (4) has only been taken to exactly sufficient places; since the coefficient 5.86 is obtained by subtraction, it may be in error by 1 unit in the last place, and therefore one more figure would be desirable. Again, in finding b from equation (3), we subtract 11.03 c from 4.545, i.e. we subtract 5.22 from 11.03. Clearly, to be sure of the second decimal place, i.e. to know b to two figures, it would be preferable to know the value of the quantity 11.03 c to one more figure. Similarly, the second significant figure of a would be more sure if c were known to one more figure*.

It is apparent that when any constant is required with greater precision than these, as is usually the case, the calculations are outside the range either of a slide-rule or of four-figure logarithms.

In the method of least squares, the amount of arithmetic required is, of course, greater even than in the method of zero sum.

§ 2. PROPOSED METHOD

It is clear from the foregoing that a simpler method of determining the constants in the equation $y = a + bx + cx^2$ would be of value. Much of the labour in the standard methods arises from the fact that the equations are added, numbers with many significant figures being thus introduced, and all the constants are determined simultaneously.

* As a matter of fact a more exact calculation shows that the values $a, b, c = 1.32, -0.67$ and 0.473 should be $1.30, -0.65$ and 0.471 , so that slide-rule accuracy introduces perceptible errors even in this case.

If any one of the constants can be determined before the others, the problem becomes much simpler. Thus if c is known first, it is easy to plot $(y - cx^2)$ against x and so to determine a and b as the intercept and slope of a straight line; if b is known, $(y - bx)$ is a linear function of x^2 , whilst if a is determined first, then $(y - a)/x$ is linear against x . (The reference to plotting does not imply that graphical methods are necessary. There are plenty of easy arithmetical methods for determining the two constants in a linear formula.)

For several reasons, the constant c is the most useful to determine first. It is often the coefficient of a small term, and the arithmetic involved in preparing the linear function to determine a and b is easily carried out. Moreover, as will be shown elsewhere, if mean values have been measured for a quantity which varies with x , it is in any case desirable to know c in order to correct these values to instantaneous values.

Fortunately c is not only the most useful constant to determine first; it is also the easiest. For consider three values of x and the corresponding values of y , say

$$y_1 = a + bx_1 + cx_1^2,$$

$$y_2 = a + bx_2 + cx_2^2,$$

$$y_3 = a + bx_3 + cx_3^2.$$

By taking the differences of the y -values and those of the x -values, and dividing, the first divided differences of y are found. They are seen to be given by

$$(y_2 - y_1)/(x_2 - x_1) = b + c(x_1 + x_2) \quad \text{and} \quad (y_3 - y_2)/(x_3 - x_2) = b + c(x_2 + x_3).$$

The second divided difference is obtained by subtracting one first difference from the other and dividing by $(x_3 - x_1)$, the range of values of x concerned in its formation. From the above equations it is immediately seen that the second divided difference is simply equal to c .

A numerical example will make the matter clear.

Table 1. Divided differences of a function

x	y	Differences of		First divided difference of y	Second divided difference of y		
		x	y		Numerator	Denominator	Value
1	9						
2	15	1	6	6			
4	33	2	18	9	9 - 6 or 3	4 - 1 or 3	1
5	45	1	12	12	12 - 9 or 3	5 - 2 or 3	1
7	75	2	30	15	15 - 12 or 3	7 - 4 or 3	1
12	185	5	110	22	22 - 15 or 7	12 - 5 or 7	1
13	213	1	28	28	28 - 22 or 6	13 - 7 or 6	1

§ 3. A NUMERICAL EXAMPLE

To show the operation of the method, the following table of corrections to the constant-volume helium thermometer will be taken, and a parabolic formula deduced to represent the results. The first column gives the temperature, the second the correction in thousandths of a degree. The working is shown in the later columns, the last of which should be a linear function of x . A plot of the figures verifies this, and consequently shows that the parabolic form is suitable for representing the data.

Table 2

x	y	Δy	$\Delta^2 y$	cx^2	$y - cx^2$
- 183	19			12.8	6.2
- 150	14	- 0.151	+ 0.00037	8.6	5.4
- 100	8	- 0.120	+ 0.00020	3.8	4.2
- 50	3	- 0.100	+ 0.00040	1.0	2.0
0	0	- 0.060	+ 0.00040	0.0	0.0
50	- 1	- 0.020	+ 0.00040	1.0	- 2.0
100	0	+ 0.020	+ 0.00040	3.8	- 3.8
150	3	+ 0.060	+ 0.00040	8.6	- 5.6
200	8	+ 0.100	+ 0.00040	15.2	- 7.2
250	15	+ 0.140	+ 0.00020	23.8	- 8.8
300	23	+ 0.160	+ 0.00060	34.3	- 11.3
350	34	+ 0.220	+ 0.00020	46.7	- 12.7
400	46	+ 0.240	+ 0.00060	61.0	- 15.0
450	61	+ 0.300		77.2	- 16.2
Mean $c = 0.000381$					

The time occupied in forming this table, including the copying out of the first two columns, was 9 minutes, of which less than half sufficed to determine c .

To determine a and b , a variety of methods is available, and we will select that of zero sum. Adding the upper halves of the first and last columns gives $12.0 = 7a - 333b$, and adding the lower halves gives $- 76.8 = 7a + 2100b$. By difference, $2433b = - 88.8$ or $b = - 0.0365$, and then $7a = - 0.17$ or $a = - 0.02$.

The time occupied in this determination of a and b was $5\frac{1}{2}$ minutes, making a total of $14\frac{1}{2}$ minutes for the whole process of determining the parabolic equation

$$y = 0.02 - 0.0365x + 0.000381x^2.$$

To solve the same problem by the method of zero sum, it is first necessary to write down the fourteen equations of which the first is

$$19 = a - 183b + 33489c,$$

and to divide these into three equal groups of $4\frac{2}{3}$ equations each*. These groups are then added, to form the three normal equations

$$\begin{aligned}44 &= a - 483b + 68,490c, \\15 &= a + 583.3b + 95,833c, \\174 &= a + 1666.7b + 616,667c,\end{aligned}$$

a process which was found to occupy 8 minutes.

If these are solved with merely slide-rule accuracy (which is not really sufficient), they give $a = -0.01$, $b = -0.0370$ and $c = 0.000382$, the time occupied being 11 minutes, making a total of 19 minutes. The difference in the results by the two methods is insignificant, although the time-difference is over 30 per cent.

In the solution by least squares, even the formation of the normal equations occupied 31 minutes, and their solution 16 minutes.

When the results calculated by the various methods are compared with the original data, each method shows a maximum deviation of 0.6 of a unit, though these deviations all occur at different values of the temperature x .

§ 4. REFINEMENT OF THE METHOD

In the example just taken, the differences of both the first and second orders were found by subtracting successive entries in the table. This was justifiable because the twelve estimates of c did not vary greatly, but in general this would not be so. This procedure does not weight the observations equally, since every y -value except the first and last enters into the calculation of two first differences. Consequently the first two and last two entries are weighted differently from each other and from the rest of the entries. Again, if the observations are scattered at all widely about the mean parabola representing them, some of the first and second differences will be reversed in sign with respect to the rest. For example, if the trend of the observations is such as to demand a parabola with its axis vertical and vertex downwards, then a single high observation lying between two normal or low ones introduces a value of c representing a parabola with vertex upwards. Again, if three observations are very close together in their x -values, they may give quite large divided first differences, and these will exercise undue weight in the second differences.

For these reasons, it is desirable to form the first differences by dividing the table into two equal halves, ignoring the middle observation if there are an odd number, and subtracting the values in corresponding positions in the two halves. In this way every observation which is used at all is used just once. The same principle is then to be extended to the second differences. Thus, supposing there are $2n$ observations the first divided differences will be

$$\frac{y_{n+1} - y_1}{x_{n+1} - x_1}, \frac{y_{n+2} - y_2}{x_{n+2} - x_2}, \dots,$$

* A fraction such as two-thirds of an equation is obtained by multiplying every coefficient by $\frac{3}{2}$. E.g. $\frac{2}{3}$ of the equation $3 = a + 6b + 36c$ is $2 = \frac{1}{3}a + 4b + 24c$.

i.e. $b + c(x_{n+1} + x_1)$, $b + c(x_{n+2} + x_2)$, ...

and the second will proceed analogously.

To illustrate the improvement effected by this refinement of the procedure, we may take an example of scattered data from Merriman's *Least Squares*, p. 140. The observations are shown and are treated by the cruder method in table 3.

Table 3

x	y	Divided first differences	Divided second differences
28	11.71	1.19/38 or 0.0313	
66	12.90	3.50/107 or 0.0327	+ 0.0014/145 or + 9.7×10^{-6}
173	16.40	3.60/75 or 0.0480	+ 0.0153/182 or + 84.1×10^{-6}
248	20.00	2.20/50 or 0.0440	- 0.0040/125 or - 32.1×10^{-6}
298	22.20	1.55/102 or 0.0152	- 0.0288/152 or - 189.5×10^{-6}
400	23.75	2.70/105 or 0.0257	+ 0.0105/207 or + 50.7×10^{-6}
505	26.45	1.25/43 or 0.0291	+ 0.0034/148 or + 23.0×10^{-6}
548	27.70		Mean - 9.0×10^{-6}

Each entry in the last column is an estimate of the constant c , and it is obvious that the mean is quite unreliable. The most favourable complexion is given to the figures by taking first the mean of the three estimates - 189.5, + 84.1 and + 50.7 (i.e. - 18.2) and secondly the mean of the other three (viz. + 0.2) and comparing these means, but it certainly gives no confidence in the final result.

If now the half-table method is adopted, the calculation takes the form given in the next table.

Table 4

x	y	Divided first differences	Divided second differences
28	11.71		
66	12.90		
173	16.40		
248	20.00		
298	22.20	10.49/270 or 0.03886	
400	23.75	10.85/334 or 0.03249	
505	26.45	10.05/332 or 0.03027	- 0.00859/(207 + 145) or - 0.0000244
548	27.70	7.80/300 or 0.02566	- 0.00683/(148 + 182) or - 0.0000207

The two estimates of c in the last column are much closer together than the two estimates obtained previously by grouping three observations together to obtain a mean, and in fact it seems probable that two-figure accuracy can be justifiably claimed in the value of c now deduced, although three would be used in practice, to avoid errors due to rounding off.

A second important point is that the value - 22.6×10^{-6} deduced for c in

table 4 not only is apparently more reliable, but is nearly three times as large as that deduced in table 3. This larger value is much nearer to the value -23.1×10^{-6} given by the method of least squares and to the value -32.2×10^{-6} given by the method of zero sum; in view of the differences between the values due to these older methods, it is to be presumed that the observations depart so far from a parabola that any value between -19 and -32 is as "true" as any other.

§ 5. DETERMINATION OF THE CONSTANTS a AND b

Attention has so far been mainly devoted to the determination of the constant c , which is all that would be required in correcting mean values to instantaneous ones. If the whole equation is to be found, the constants a and b will be required, and many methods are available for determining them.

In one of the examples given above the quantity $y - cx^2$ was formed and zero sum then utilized. This is a convenient method since it easily gives two equations for the two unknowns, one of which is immediately eliminated by subtraction. An equally simple method, and one which gives a visible check on whether a parabolic equation is in fact satisfactory, is to form as before the quantity y' which $= y - cx^2 = a + bx$. The half-table method is then used to determine b , which is given as the ratio between the differences of y' and of x . When b has been determined, an estimate of a is obtained from each observation by subtracting bx from the previously tabulated quantity y' . The deviations of these estimates of a from their mean are identically equal to the deviations of the calculated values of x from the observed values, and this is a valuable feature of this method of determining a and b .

Yet another method of determining a and b is available. In the process of finding c , first divided differences are formed and are equal to $b + c(x_r + x_s)$. Hence by subtracting the appropriate value of $c(x_r + x_s)$ from each divided difference, a number of estimates of b are obtained.

These methods are illustrated for the problem from Merriman just dealt with, table 5 showing the half-table method.

Table 5

x	y	x^2	cx^2 ($c = 22.6$ $\times 10^{-6}$)	y'	b	bx ($b = 0.0434$)	a or $y' - bx$
28	11.71	780	0.02	11.73		1.22	10.51
66	12.90	4360	0.10	13.00		2.86	10.14
173	16.40	2930	0.68	17.08		7.51	9.57
248	20.00	61500	1.39	21.39		10.76	10.63
298	22.20	88800	2.01	24.21	12.48/270 or 0.0412	12.93	11.28
400	23.75	16000	3.61	27.36	14.36/334 or 0.0430	17.36	10.00
505	26.45	255020	5.76	32.21	15.13/332 or 0.0456	21.92	10.29
548	27.70	300300	6.78	34.48	13.09/300 or 0.0436	23.78	10.70
Mean					0.0434	Mean 10.39	

* The result quoted in Merriman's book is not the least-squares result to the problem worked out here. It is the conditioned solution forced to pass through the point representing the surface temperature.

The first-divided-difference method is set out in table 6.

Table 6

x	First divided differences	$(x_r + x_s)$	$c(x_r + x_s)$	b	bx ($b = 0.0446$)	$y - cx^2$	a
28					1.25	11.73	10.48
66					2.94	13.00	10.06
173					7.72	17.08	9.36
248					11.05	21.39	10.34
298	0.03886	326	- 0.0074	0.0463	13.29	24.21	10.92
400	0.03249	466	- 0.0105	0.0430	17.84	27.36	9.52
505	0.03027	678	- 0.0153	0.0456	22.51	32.21	9.70
548	0.02566	796	- 0.0180	0.0437	24.42	34.48	10.06
			Mean	0.0446		Mean	10.06

We have thus a number of alternative equations, each purporting to represent the data:

From least squares

$$10.21 + 0.0442x - 23.1 \times 10^{-6}x^2;$$

from zero sum

$$9.75 + 0.0495x - 32.2 \times 10^{-6}x^2;$$

from the difference method, using the half table to determine b ,

$$10.39 + 0.0434x - 22.6 \times 10^{-6}x^2;$$

from the difference method, using the first divided differences to determine b ,

$$10.06 + 0.0446x - 22.6 \times 10^{-6}x^2.$$

The accuracy of these various equations can be estimated by calculating y from each at the given values of x , and noting the deviations between the observed and calculated values of y . The main results of such a comparison are shown in table 7, from which it will be seen that in point of fidelity to the data there is little to choose between the various methods.

Table 7

	Least squares	Zero sum	Difference method	
			Half table	First differences
Average deviation	0.40	0.43	0.39	0.40
Maximum deviation	0.87	0.96	0.82	0.86
Sum of squares of deviations	1.84	2.27	1.85	1.90

DISCUSSION

Dr FERGUSON. It is all very well to discourse opulently of reductions made in five or ten minutes with the aid of mechanical computers, but those of us whose normal equipment consists of a thirty-centimetre boxwood rule, a few pieces of squared paper of doubtful rectangularity, and a well-thumbed copy of Bottomley,

do not disdain more primitive methods which will achieve a result in something less than half an hour.

In handling an equation of the type considered by Mr Awbery,

$$y = a + bx + cx^2,$$

if we plot the best xy curve, take a point x_0y_0 thereon, and transfer the origin to this point we can, by plotting the new values of y/x as ordinate against x as abscissa, obtain a straight line the slope and intercept of which determine c and b .

Having found these constants, from each pair of original values of y and x we can determine a value of a by using the original equation.

This method of reducing a four-term equation to what is practically a three-term form by transferring the origin to a point on the curve is certainly restrictive, but it is simple, of fairly general application, and it obeys the pragmatic test.

Mr T. SMITH. From an examination of the outstanding errors in a number of problems when formulae have been fitted by least squares, by the method of this paper, and by others, the conclusion emerges that this method tends to give solutions which approach very nearly—certainly more closely than other methods included in the comparison—to the least-squares solutions but with much less labour than the latter involve. The method ought therefore to prove particularly valuable where a simple, rapid and reliable method in which weight is given to all the observations is required.

AUTHOR'S reply. I sympathize with Dr Ferguson's plea for the man whose study is not well equipped with aids to computing, but surely the fact that the squared paper is of doubtful accuracy should be an argument against, rather than for, graphical methods? I am an advocate of reducing numerical work where possible to the determination of the parameters of a straight line, but I prefer to determine them arithmetically, using the eye only as a safeguard against the adoption of an unsuitable formula, or the introduction of a gross mistake.

My objections to Dr Ferguson's procedure in the particular case of a quadratic formula are centred around the selection of a point (x_0, y_0) through which the curve is forced to pass. I feel that this selection may bias the whole curve, and further that the selection may be no simple matter. Consider the example in table 2 of Mr Smith's paper*. Here, values of v range from 2.97 to 3.20 and are given to four decimal places. If they are plotted so that 1 cm. represents 0.01 of a unit (a curve 9 inches wide), then to estimate the fourth figure in v_0 requires reading the curve to the nearest tenth of a millimetre. I presume Dr Ferguson would surmount this difficulty by plotting, not the observations, but their deviations from a straight line passing through the third and eighth points; but if so, there is quite considerable labour to be done before he starts the main process.

* Page 566 of this volume.

REVIEWS OF BOOKS

The General Principles of the Quantum Theory, by G. TEMPLE. Pp. viii + 120.
(London: Methuen & Co., Ltd.) 3s.

Methuen's monographs on physical subjects, to which series this booklet belongs, are mostly excellent value, and the present one is certainly no exception to the rule. It introduces the student to all the main conceptions of modern quantum theory, and does not omit to show him how to work the mathematical apparatus which has been adopted in this branch of theoretical physics.

To do all this in the space available would be impossible without tremendous compression, and the book is therefore difficult reading. Of necessity, the arguments are mainly expressed in mathematical symbolism, and explanations as to how one equation follows from another have been kept to a minimum.

Nevertheless, it can be read by any conscientious student, and he can assure himself that his knowledge is real and not superficial by working the examples. These add greatly to the value of such a work as this, and make it more valuable as an introduction to the subject than works of many times the size with no examples. There are one or two misprints in them, as on p. 11, ex. 2, where the replacement of "are" by "and" makes it look as if the enunciation is incomplete. The other misprints (two on p. 41 and several in chapter 5) are even more trivial.

It is refreshing to find an author who considers that English is good enough for him. For once, we find a book on quantum theory in which "characteristic" is not rendered as "eigen," nor "trace" as "spur."

J. H. A.

Wave Mechanics. Advanced General Theory, by J. FRENKEL. Pp. viii + 525.
(Oxford: Clarendon Press.) 35s.

This is the second volume of a trilogy, of which the first dealt with elementary general theory and the third will treat special problems in detail.

The distinction between the elementary theory of the first volume and the advanced theory of the one under review is very marked. Here the relationship to classical mechanics is developed from the most refined formulation of the latter subject, and the equations of the new mechanics are built up in the first place as generalizations of classical mechanics with operators taking the place of quantities. In this synthesis, the analogy between classical mechanics and geometrical optics on the one hand, and wave mechanics and undulatory optics on the other, is not used at all.

The development by which the operators are represented as matrices is next taken up, this part of the subject being completed on p. 126.

The next two chapters are devoted to the transformation theory. Here we are given two operators H and K , representing the energy of a particle in two fields of force with different potential energies, and are required to find what relations exist between the characteristic functions ψ_H and ψ_K , and also between the two matrices which represent a given operator E , in its relation first to H and then to K . The perturbation theory is a special case, where the energies H and K are related so that one is an approximation to the other.

This brings us practically half way through the book, and the remainder is much more difficult reading. It opens with a chapter on "relativistic remodelling and magnetic generalization of the wave mechanics of a single electron." This chapter, of course, introduces the spin effect and is well written to show the way in which the magnetic

generalization is indissolubly linked to the relativistic outlook. After it comes the problem of many particles, and the treatment by what is variously known as second quantization, super-quantization or intensity quantization.

This second half of the book contains much that is very recent, and naturally has to deal with problems where the best solution that can be given is known to be incomplete or incorrect. In the main it follows the treatment given by Dirac in his various papers, though there is no slavish adherence to any one line of discussion. It will be seen that the term "wave mechanics" is used in a very wide sense, and includes modern quantum electrodynamics.

As a whole the book is difficult reading. In many ways it is reminiscent of Thomson and Tait's *Natural Philosophy*. Both books adopt an extremely general outlook, though the older one is kinder in giving examples (even trivial ones are helpful) of the sort of system to which any given theorem applies. This is balanced by the greater discursiveness in Frenkel's book, and in particular by the lengthy verbal translations which frequently precede the mathematical investigations.

The books have another similarity—their weight and general unsuitability for armchair reading. In the present case this is due partly to the very thick paper which the publishers have provided. They and the printers are to be congratulated on the excellent production of a book which must have been extremely difficult to set up. The mathematical portions abound with cases where a symbol carries a subscript which itself bears a subscript or a prime or both, whilst double superscripts like 1^* or 0^{1*} or $0^{(1)}$ are frequent. Despite this complexity only three or four examples of misprints have been noticed, none of them important enough to require citation.

J. H. A.

L'Électron Magnétique (Théorie de Dirac), by LOUIS DE BROGLIE. Pp. viii + 316. (Paris: Hermann et Cie, 1934.) 100 fr.

Although Dirac's theory of the electron is usually regarded as one of the high peaks of achievement in mathematical physics, probably few physicists would claim to have more than a vague appreciation of its general character. A full understanding of the theory requires not only a thorough grasp of the spirit of quantum mechanics and of relativity, but also familiarity with a difficult mathematical technique.

Dirac's equations for the electron are arrived at by modifying the usual relativistic wave equation in such a way as to meet a postulated formal requirement that the equations shall be of the first order in time. From the aesthetically satisfying equations so built up may be deduced consequences, in agreement with experiment, as to spin and magnetic moment; so that these appear not as fundamental irrationals, but as particular aspects of a wider scheme.

The essence of the theory is given, with amazing economy of symbolism, in the last chapter of Dirac's *Quantum Mechanics*. De Broglie gives a fuller presentation, leading up by gradual steps from what will be familiar to many physicists to the more recondite theory.

In the first part of the book there is a good survey of the relevant parts of classical quantum theory and of wave mechanics. The second part deals with the Dirac theory, with due reference to the earlier work of Pauli and Darwin. The arguments of Dirac are presented in a manner which will be appreciated by those who wish to gain a clear impression of the nature of the theory without working through the detailed mathematical development which follows. This part of the book concludes with a formidable table of the sixteen hermitic operators involved in the theory, together with expressions for the operators corresponding to mass, charge, current, magnetic and electric moment, and spin.

The third part of the book deals with applications, and the theory of fine structure and of the Landé g factor is fully worked out for the one-electron case. The theory

suggests not only magnetic moment and spin, but also an imaginary electric moment, and the possibility of states of negative energy (mass) for the electron. These are briefly discussed, as also questions connected with the lack of symmetry in the appearance of space and time coordinates in the equations.

De Broglie's book is an admirable piece of detailed and lucid exposition which will be of value both to those hesitantly approaching the Dirac theory, and to those requiring a systematic account of it. The book is well printed, and it is adorned with a plate of X-ray spectra and attractive, if irrelevant, head and tail pieces to the chapters showing fragments of line and band spectra.

E. C. S.

Atomic Theory and the Description of Nature, by NIELS BOHR. Pp. 119. (London: The Cambridge University Press.) 6s. net.

It was a happy thought to bring together five classical essays by Prof. Bohr. Two of them, *Atomic Theory and Mechanics* and *The Quantum Postulate and the Recent Development of Atomic Theory* are familiar to English readers, having appeared in *Nature* in 1925 and in 1927 respectively. The remaining essays are for the first time translated into English. *The Quantum of Action and the Description of Nature* appeared in German in 1929, while *The Atomic Theory and the Fundamental Principles underlying the Description of Nature* was published in Danish in the same year. The fifth essay, entitled the *Introductory Survey*, was published in Danish in 1929, and carries an *Addendum* which was included in the German edition (1931) of a volume which comprised the four articles just named. Description of and comment on these articles are unnecessary, and the convenience of having, in the compass of a small volume, such masterly surveys of the physical thought of the time needs no emphasis.

The historical value of the present volume will be enhanced by the later appearance of a companion volume "containing a number of later essays on the same subject, in which the general point of view is further developed."

A. F.

The Atom, by JOHN TUTIN, D.Sc. Pp. 103. (London: Longman's Green & Co., Ltd.) 6s. net.

Dr Tutin desires to flype the atom—to give us a structure with the massive protons circulating round a light nucleus. This may seem to some a difficult matter to envisage, but, as Dr Tutin sagely says, "a flywheel with a heavy rim and a light hub is a far more commonplace conception than a flywheel with a light rim and a heavy hub."

He accomplishes his ingenious little essay without any display of mathematical learning, and consequently has not a great deal to say concerning modern spectroscopy. Read critically, the volume will provide a useful exercise in dialectic for a physics student in the honours grade.

A. F.

Molecular Hydrogen and its Spectrum, by O. W. RICHARDSON. Pp. xiv + 343. (New Haven: Yale University Press, 1934.)

As the subject of the Silliman Lectures delivered by Prof. Richardson at Yale University in April 1932 and now appearing in book form none, surely, could be more fitting than this complicated spectrum, in the analysis of which the lecturer and his co-workers have taken such an outstanding part extending over about a decade. Having before us a fair-sized book entirely devoted to one spectrum and its emitter, we may well understand the amazement and the doubt expressed by some spectroscopists of sixty to seventy years ago that this complex mass of lines of the so-called "secondary" or "many-lined" spectrum could be associated with the lightest of the chemical elements. The fundamental importance of

the spectrum in present-day physics is rooted in the fact that its emitter, H_2 , the simplest of all molecules, is a structure which the earlier quantum theory entirely failed to interpret but which has been successfully dealt with by the more difficult methods of the new quantum mechanics. Of the many tests which the latter has passed in practical band spectroscopy and other fields none perhaps could be severer than that supplied by a comparison of the theoretical and the observational data for the H_2 spectrum.

The authoritative, critical and logically connected account given here will be especially valuable to all students of this difficult subject because the original papers in which the analysis and interpretation of the spectrum have been unfolded are so numerous and so scattered, and also because the book contains a considerable amount of matter which has not hitherto been published and is not intended for publication elsewhere.

The first two of the ten chapters deal with the new quantum-mechanical theory of a pair of nuclei with one electron and with two electrons, in particular the H_2^+ ion and the neutral H_2 molecule. The general theory of molecular states and spectra is outlined in chapter 3, which deals with transition probabilities, symmetry properties, effects of spins of electrons and nuclei, selection rules, structure of a band system and of a band, and an outline forecast of the H_2 spectrum. The next five chapters are devoted to the detailed analysis of the H_2 spectrum, one to the singlet systems in the far ultra-violet, two to the singlet systems in the less refrangible regions, and two to the triplet systems. The subjects treated in chapter 9 include molecular energy functions, intensity-distribution, uncoupling phenomena, specific heat of hydrogen, the Raman spectrum of H_2 , and the H_2 continua. The final chapter comprises a section on the theory of the excited states of H_2 , a discussion of the experimentally established electronic levels, an account of the spectral variations with different conditions of excitation, and a most valuable and comprehensive table of numerical constants for all the known electronic states of H_2 and H_2^+ .

It is particularly fortunate that this masterly work has appeared just when the results of the analysis of the H_2 spectrum are being used in connexion with the analyses of the spectra of the isotopic molecules HD and D_2 (i.e., H^1H^2 and H_2^2) which, of course, were not recorded at the time Prof. Richardson delivered these Silliman lectures and wrote them for publication in book form.

W. J.

Exploring the Upper Atmosphere, by DOROTHY FISK. Pp. 166. (London: Faber & Faber, Ltd.) 6s. net.

One of the most fascinating stories of the century is that of the growth of our knowledge concerning the upper atmosphere; it presents an almost incredible combination of Jules Verne-like fantasies, of human daring, modern atomic physics and recondite technical equipment.

The scope of Miss Fisk's essay may be adequately indicated by a summary of her chapter-headings—Ballooning, Through the troposphere to the lower stratosphere, Sound as an explorer, Ultra-violet rays and the ozone layer, The paths of radio-waves, Projectiles in space, Polar lights and cosmic rays.

The book is intended to appeal to the layman. The author writes in a clear and light-hearted style and has produced a useful elementary introduction to a difficult subject.

A. F.

Ocean Waves, by VAUGHAN CORNISH. Pp. xv + 163. (London: The Cambridge University Press.) 10s. net.

Physics is not to be regarded as primarily an observational science, and its devotees not infrequently show themselves to be singularly lacking in those powers of rapid, complete and accurate observation which form an essential part of the equipment of a

successful naturalist. "I didn't notice it" comes as naturally from the lips of a physicist as from the most Hegelian of metaphysicians.

Dr Vaughan Cornish has provided us with a very valuable study of the size and speed of ocean waves in relation to wind velocity, of waves in sand and snow, and of tidal bores and allied phenomena; and he has demonstrated very clearly what can be accomplished by keen and careful observation plus a certain amount of measurement made with the simplest tools. He has adorned his book with a series of most beautiful photographs of the waves which he describes so lucidly and enthusiastically.

Dr Harold Jeffreys can always be depended on to be clear and terse; the appendix which he contributes is the best short elementary survey known to the present writer of certain aspects of surface wave phenomena.

A. F.

L'Excitation Électrique des Tissus, by A. M. MONNIER. Pp. xvi + 326. (Paris: Hermann et Cie, 1934.) 85 fr.

To explain the wide range of known excitability phenomena the author makes the following two fundamental assumptions: (a) a tissue will attain a threshold excitation when the excitatory process E reaches a fixed value E_0 ; (b) E is related to the chronaxie τ , the stimulating current I and the time t by the equation

$$a\tau \frac{d^2E}{dt^2} + b \frac{dE}{dt} + \frac{c}{\tau} E = \frac{dI}{dt},$$

where a , b , c are constants independent of the nature of stimulus or tissue.

Experimental results are compared in detail with the solution of this equation for over a score of different functions of I with respect to t . In nearly all cases there is good qualitative agreement, but it is doubtful whether the lack of quantitative correspondence justifies so minute a treatment. A significant fraction of the 300 pages is virtually a re-statement, since the quantitative details are too remote from fact to be of importance. On the other hand this very detail, supported by a full bibliography, constitutes a valuable source of reference to the temporal aspects of tissue-excitation.

The author approaches the subject from the standpoint of Lapicque's school, and makes an interesting attempt to give a quasi-physical basis to the tenets of that school upon the phenomena of curarization, summation, central inhibition and facilitation, and irreciprocal conduction. Particularly satisfying is it to find that the author is careful to collect the observations which oppose his theory as well as those which illustrate it. These objections are briefly discussed and plausible explanations are offered.

Thus Monnier's theory on the one hand brings under a single concept a very great mass of facts, and on the other it points to the exceptions as phenomena which demand further investigation both theoretically and by experiment.

W. A. H. R.

Free Radicals. A General Discussion held by the Faraday Society, September, 1933. Pp. 248. 12s. 6d.

The present discussion covers a large amount of ground and various aspects of the subject receive treatment. Thirty separate communications, on many of which there were discussions, appear, so that it is impossible even to state the titles of all the papers contributed. The discussion was divided into two main sections: (i) free radicals of relatively long life, which included papers on the electronic structure and interaction of some simple radicals, the electronic levels of polyatomic molecules, and three dimensional models of the potential energy of triatomic systems; and (ii) free radicals of short life, subdivided into the chemical aspects, hydrocarbons, and the physical aspects, this part being subdivided into three sections. These sections included several subjects of interest to physicists

such as free radicals produced in electric discharges and free radicals in spectroscopy. A paper on the application of molecular rays, however, is very brief and is mainly suggestive of future work. The use of positive rays in detecting free radicals, one of the oldest physical methods, is represented by a paper on the products of decomposition of some hydrocarbons, the chemical aspects of the thermal decomposition and combustion of hydrocarbons being also represented. Many of the papers deal with interesting theoretical aspects of the subject. This discussion, which was held at Cambridge, proved very interesting and fruitful and the resulting volume is one which contains many accounts of new work as well as critical discussions of results already known. The great advances which have been made in recent years in the study of the subject from many different points of origin are clearly apparent, and the volume is one of unusual interest and importance. Physicists who are interested in molecular structure and spectroscopy, in particular, will find in it much of interest.

J. R. P.

Scientific Inference, by HAROLD JEFFREYS, F.R.S. (London: The Cambridge University Press.) 10s. 6d.

At the present time, when theories of measurement and the possibility (or impossibility) of the measurement of certain magnitudes is a matter of controversy, it is desirable to draw attention to Dr Jeffreys's valuable volume on scientific inference. The topics which he discusses are of vital interest to all physicists who occupy themselves with the philosophy of their subject, and his treatment of probability, sampling, quantitative laws, errors, physical magnitudes and mensuration is equally provocative and lucid.

His work is of wider range than this restricted catalogue would indicate; he is, in fact, primarily concerned with the principle that it is "possible to learn from experience and to make inferences from it beyond the data directly known by sensation," and, adopting this principle as a primitive postulate, has developed its consequences in various directions.

The argument is, as always with Dr Jeffreys, brilliantly clear, and is enlivened by the aptest and wittiest of illustrations. Who but the author would have seized on the immortal quatrain of Messrs Layton and Johnstone

"Oh, it ain't gonna rain no mo', no mo',
It ain't gonna rain no mo'!
How in the hell can the old folks tell?
"Tain't gonna rain no mo'!"

and employed it to head, most appropriately, a chapter on probability?

A. F.

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NOTES ON THE PRESSURE OF RADIATION

By G. F. HULL, Professor of Physics, Dartmouth College, U.S.A.

AND

MARY BELL, A.R.C.S., B.Sc., AND S. E. GREEN, Ph.D.

Read June 1, 1934.

ABSTRACT. § 1 consists of a brief account of some early experiments on radiation pressure, dealing in particular with the investigations of Lebedew and of Nichols and Hull. In § 2 Dr Hull reconsiders some aspects of his work, in view of the errors of calculation pointed out in these *Proceedings* by Mary Bell and S. E. Green. In § 3 the latter authors reply to Dr Hull's note.

§ 1. A RÉSUMÉ OF SOME EARLY EXPERIMENTS ON RADIATION PRESSURE

By S. E. GREEN, Ph.D.

Received March 20, 1934.

Introduction. The phenomenon of radiation pressure is of considerable importance in modern science, more particularly in astrophysics, where it constitutes a prominent factor to be taken into account by astronomers in speculations concerning the state of heavenly bodies. The search for the existence of the phenomenon in the case of terrestrial sources of light has an interesting history.

Although experiments successful in detecting the pressure of radiation have been confined to the present century, this pressure has been the subject of research since comparatively early times. The idea that light could exert a pressure seems first to have been advanced by Kepler*, who in 1619 thereby explained the repulsion of comets' tails by the radiation of the Sun. In the middle of the eighteenth century De Mairan and Dufay† conducted laboratory tests. The emission theory of light being then generally accepted, a pressure due to radiation incident upon a receiving surface was to be expected from the arrest of the flying corpuscles. The results obtained were, however, quite inconclusive. The subject was subsequently

* De Mairan, *Traité Physique et Historique de l'Aurore Boréale*, p. 357 (2nd edition. Paris, 1754).

† De Mairan, *loc. cit.* p. 371.

taken up by a number of investigators including Fresnel in 1825, Crookes, commencing in 1874, and Zöllner at about the same time. Fresnel* was merely able to show that the forces he observed were not of electric or magnetic origin, while in the other cases no definite detection of the pressure of radiation resulted. This is not surprising in view of the extreme smallness of the effect sought for†, together with the relatively enormous gas action which was generally produced, owing to the heating of the body receiving the radiation. Crookes's‡ interest in the subject led to the invention of his well-known radiometer, while Zöllner§, who used somewhat similar apparatus, calculated that under certain circumstances gas effects could give rise to forces many thousands of times greater than that of the radiation pressure to be expected.

Maxwell|| in 1873 had given a new impetus to the search by his deduction that if light be an electromagnetic wave phenomenon, there exists in a beam a pressure which is exerted in the direction of travel and is of magnitude numerically equal to the energy per unit volume of the beam. It followed that the total pressure exerted on a normally reflecting surface should be equal to the sum of the energy-densities of the incident and reflected beams. A few years later, Bartoli¶ established independently from thermodynamical reasoning that radiation should exert such a pressure, but failed, in common with all previous observers, in the attempt to detect and measure the pressure, owing to gas action in his apparatus.

The definite detection of radiation pressure, under conditions in which extraneous gas effects are fairly small and not dominant, has been achieved only during the last thirty years or so. During this period a few attempts have been made to test the validity of Maxwell's relation directly by separate measurement of the pressure and energy-density of radiation. The common method adopted in the case of the pressure has been to direct a stream of radiation normally upon a delicately suspended vane forming the arm of a torsion balance. Then, if gas action be absent, the pressure P due to the incident beam follows from the relation $(1 + m) PrA = c\theta$, where m is the reflecting power of the vane, A the area of the spot of light on the vane, r the arm at which the pressure acts and c the torsional constant of the suspension. The energy-density of the radiation has generally been found by the calorimetric method of observing the rise of temperature produced by the incidence of the beam upon a body of known thermal capacity. -

The main gas effects which may occur are convection and radiometer action. The usual practice has been to evacuate the containing vessel as far as possible in order to reduce gas action to a minimum. In the experiments described below Lebedew sought to eliminate this action entirely by suitable construction of the vanes, while Nichols and Hull, whose investigation was unique in the use of an unexhausted chamber, attempted to get rid of gas effects by a ballistic method.

* *Ann. de Chim. et de Phys.* 29, 57, 107 (1825).

† In the case of a beam of sunlight the pressure amounts to less than 10^{-4} dyne/cm².

‡ *Phil. Trans.* 164, 501 (1874); 169, 243 (1878); 170, 87 (1879).

§ *Pogg. Ann.* 180, 154, 296, 459 (1877).

|| *Treatise on Electricity and Magnetism* (Oxford, 1873).

¶ *Sopra i movimenti prodotti della luce e dal calore* (Florence, Le Monnier, 1876); Exner, *Rep. d. Phys.* 21, 198 (1884).

Lebedew's experiments. Lebedew's work, published at the beginning of this century* is of great importance as being the first investigation to give positive results. The torsion system having a glass fibre was mounted within a flask 20 cm. in diameter. A number of vane systems were used of which that shown in figure 1 is an example. The arm r was about 1 cm. long. The vane materials adopted were platinum, aluminium and nickel, with blackened surfaces in some cases. The source of radiation was an arc lamp O , the light from which could be directed upon either surface of any vane within the flask K by means of the optical system, duplicated in part, shown in figure 2. Variations in the intensity of the source were corrected for by reflecting a portion of the beam on to a thermocouple system L . The response of the galvanometer in circuit with the latter was recorded simultaneously with the deflections of the suspension.

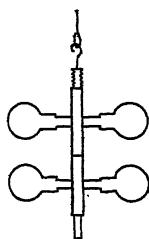


Figure 1.

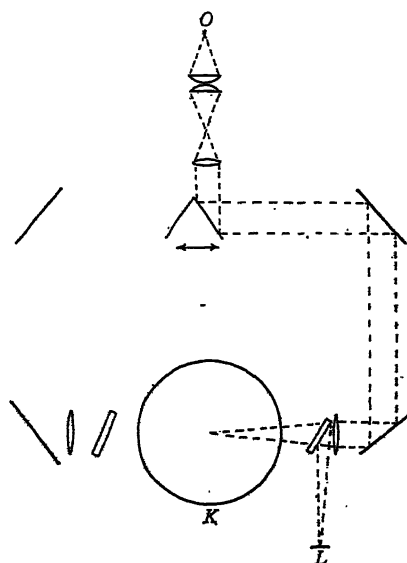


Figure 2.

Lebedew attempted to evacuate the flask down to the vapour pressure of mercury at the temperature of a freezing-mixture of ice and salt, so that the residual gas pressure was probably of the order of 0.0001 mm. He argued that convection effects would be small at such a pressure, and could be nullified by making the vanes as vertical as possible and letting the radiation fall upon each side in turn. Further the attempt was made to eliminate radiometer action by using vanes of different thicknesses and deducing the deflections for infinitely thin vanes. Lebedew does not give many deflectional data in his account, but it appears that the angular rotations of the suspension, read by means of a mirror on the stem and a scale some distance from the flask were about 0.4° . Owing to the vacuum, the suspension was in continual oscillation, the mean position being derived from the end points of the swings. The torsional constant of the suspension was found from the change in

* *Ann. d. Phys.* (4) 6, 433 (1901).

period produced by the addition of a body of known inertia. The normal period was about 5 sec. The reflecting powers of the vane-surfaces were measured by means of a photometer.

For determinations of the energy-density of the beam, the whole projection system was moved along a slide so that the radiation could be directed upon one face of a copper block, the rise in temperature of which was registered by a mercury thermometer inserted through the upper face. The water equivalent of the block was about 3 gm. A piece of glass was placed in front of the calorimeter to compensate for the presence of the side of the flask during the pressure-observations. In the later experiments the copper block was enclosed within a constant-temperature bath. From simultaneous readings of the deflections of the galvanometer in circuit with the thermocouple system *L*, figure 2, the energy-density was deduced for the standard beam, for which the value was about 25×10^{-6} erg/cm². The standard incident beam for both pressure- and energy-measurements was that which corresponded to a deflection of 100 divisions on the galvanometer scale.

Lebedew admits the possibility of errors of 20 per cent in the determinations. Owing to the great diminution of the intensity of the radiation, observations which were taken with coloured light are less reliable than those taken with full radiation. Even in the latter case the final results for the ratio of pressure to energy-density appear to have varied from 0.6 to 1.4. Much of the inconsistency probably arose from uneliminated gas action. Later observers have found rather large radiometer effects to occur at about the gas pressure used by Lebedew, but in the specimen table of deflections given it appears, from the constancy of the turning points, that in that particular case gas action was not very prominent. The marked degree of success which Lebedew achieved may in large measure be attributed to his use of thin metal vanes. Considering the small deflections of the suspension, and the comparatively rough method of determining the energy-density of the radiation, precise measurements were not to be anticipated. Although Lebedew's results are only to be regarded as qualitative, his work constituted a very great advance beyond any previous to it, in giving positive results of the right order.

The experiments of Nichols and Hull. The best known investigation on the subject is that of Nichols and Hull*, who used great ingenuity and experimental skill in an attempt to obtain a quantitative test of Maxwell's relation. For vanes they used cover glasses silvered on one side. These were supported at the base of the suspension, which was mounted within a bell jar 11 cm. in diameter, figure 3. The suspending fibre was of quartz. A rough plan of the apparatus is shown in figure 4. Radiation from the arc lamp *O* was brought to a primary focus by a lens system *S*₁, and to a secondary focus, in the plane of the suspension, by the lens *S*₂. By placing the latter against the stops *p*₁ and *p*₂ in turn, the light could be directed on to either of the vanes as required. The deflections of the suspension were observed by means of a telescope and scale *T*₂ and a small mirror *i* on the suspension. To obtain deflections with the radiation incident upon both the glass and the silvered surfaces of each vane, the suspension was rotated through 180° by turning the control magnet

* *Proc. Amer. Acad.* 38, 559 (1903); *Phys. Rev.* 17, 26, 91 (1903).

M outside the bell jar, a magnet g , figure 3, being mounted on the upper part of the suspension for this purpose. The same means was used to turn the vanes out of the way when the arm, about 0.8 cm. long, at which the radiation operated was being measured, this measurement being made by observing, through the travelling telescope T_1 , the two positions of the spot of light produced in the plane of the suspension. The torsional constant of the balance was computed from its period and its calculated moment of inertia.

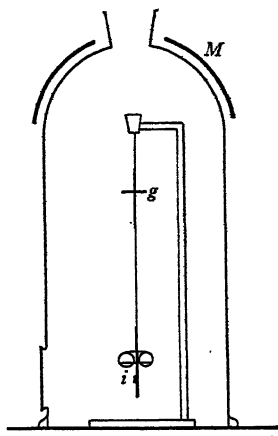


Figure 3.

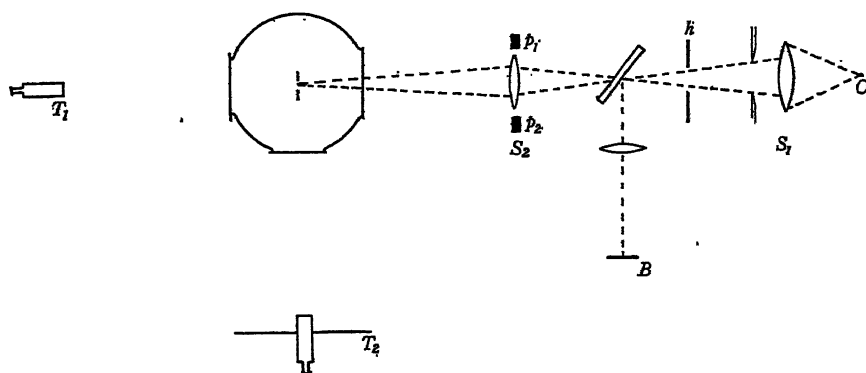


Figure 4.

A remarkable feature of Nichols and Hull's experiments was the relatively high gas pressure employed in the torsion chamber. Taking as a guide the fact that, whereas radiation pressure acts instantaneously, gas action takes time to develop, Nichols and Hull concluded, from a preliminary series of tests in which radiation was directed upon the vanes for various intervals of time, that gas action was at a minimum in their torsion chamber at a pressure of about 16 mm. of mercury. The bulk of the main experiments were then conducted at this pressure. Under these circumstances the damping of the motion of the suspension was large and care had to be taken to make the vanes vertical, otherwise the balance was very sensitive to

convection currents. Further, Nichols and Hull directed the radiation upon each vane, not permanently, but for a few seconds only. They argued that any gas action which might develop in the former case would not have time to do so in the latter. The shutter h was operated by a magnetic escapement governed by the seconds contact of a standard clock, so that the radiation could be allowed to fall upon the vane for any integral number of seconds. The selected time of exposure was six seconds, one quarter of the balance period. With the radiation incident for this interval only, the suspension being initially at rest, the first maximum deflection of the vane system was observed. The throw on the scale T_2 , about one metre distant, was roughly 30 mm. The corresponding steady deflection, deduced by calculation, was about 16 mm. for the standard beam, referred to later.

The reflecting-powers of the vane-surfaces were determined by the use of a bolometer. During the pressure-measurements the silver surfaces deteriorated rapidly* and required frequent renewal. To obtain representative average values of the reflection coefficients, observations were made on a number of fresh silver coatings deposited on the same vanes. The mean reflecting power on the silvered sides was 92 per cent and on the glass sides 78 per cent. Thus the reflecting powers of the surfaces actually used in the pressure experiments were never measured.

The energy-density of the radiation was found by removing the bell jar and directing the beam upon the blackened surface of a silver disc of known thermal capacity. The rate of temperature-rise of the disc was measured as it passed through the temperature of its surroundings. For this purpose two insulated thermocouples were inserted into the disc, which was enclosed within a water jacket provided with a suitable orifice to admit the radiation. The couple leads, suspending the disc, passed upwards through a flat wooden box into a lagged can containing kerosene in which the constant-temperature junctions were immersed. The thermocouple systems were connected in series, together with a 1000-ohm resistance and a galvanometer G_1 . The circuit was calibrated by immersing the disc in baths having temperatures a few degrees above and below that of the laboratory. The opening to the disc chamber was covered by a piece of plate glass similar to that comprising the windows of the bell jar. The disc was cooled before being enclosed by the water jacket, and the radiation was then allowed to fall upon it. The energy-density of the beam was deduced from the subsequent rate of change of deflection of the galvanometer G_1 . The slight imperfection in the absorptive power of the disc surface was allowed for, but lag of the galvanometer and of the thermocouples seem to have been disregarded. It is uncertain, however, how far the claim to a final accuracy of $\frac{1}{2}$ per cent was justifiable†, in view of the use of mercury thermometers to measure all the necessary temperatures and of the neglect of lag effects, which to some extent must occur in all variable-state methods.

The circuitous experimental methods made the evaluation of the final results very involved. In a manner similar to that adopted by Lebedew, Nichols and Hull

* Nichols and Hull state that during their preliminary experiments the silvered surfaces rarely lasted for more than two evenings' work.

† Apart from the error in the mechanical equivalent of heat, referred to later on page 596.

attempted to correct for fluctuations in the intensity of the source of light by reflecting a fraction of the radiation by means of a glass plate on to a suitable receiver. The latter was the bolometer *B*, figure 4, in circuit with which was a second galvanometer G_2 , the deflections of which were recorded during both the pressure and the energy-density observations. All results were then reduced to the values relating to a constant permanently incident beam of standard intensity, the beam being chosen so as to produce a steady deflection of 100 divisions on the scale of galvanometer G_2 .

It is to be noticed that during the pressure-measurements, owing to the short exposures used, Nichols and Hull observed not steady deflections but ballistic throws of both the vane system and the galvanometer G_2 . From the throw of the torsion balance was derived the displacement α at which the couples due to the radiation and the elasticity of the fibre would be equal. This required the division of the observed throw by a calculated factor F of about 1.3. Then, by means of an experimentally determined correction amounting to 50 per cent, the ballistic throw of the galvanometer G_2 was converted to the steady deflection δ which would be produced by the same beam if incident permanently. The assumption was made that the radiation pressure was proportional to the intensity, and the deflection of the torsion balance corresponding to the standard incident beam was then $100\alpha/\delta$. Nichols and Hull did not perform their calculation in this order, but the above description affords a simple way of explaining the nature of the reduction which they carried out.

An additional complication arose from the fact that the sensitivities of the galvanometers which were both of the moving magnet type, varied and needed to be checked continually. One cause of disturbance was the rotation of the control magnet *M* outside the bell jar. Nichols and Hull had therefore to reduce all their values of pressure and of energy-density to correspond to standard sensitivities of the galvanometers*, before deriving results relating to the standard incident beam.

The ultimate comparison took the following form. The total radiation pressure due to the incident and the reflected components of the beam was compared with $(1 + m)$ times the energy-density E of the standard incident beam. The final figures given by Nichols and Hull were as shown in table 1.

Table 1

Total pressure (10^{-5} dyne/cm ²)	$1.85E$ (10^{-5} erg/cm ²)	Difference (per cent)
7.01 (± 0.02)	7.05 (± 0.03)	- 0.6

In addition to observations for the full radiation from the arc lamp, two further sets of readings were taken with the same radiation after it had passed through ruby glass and through a water cell. The final figures for the latter two cases are not quite

* Although not definitely stated to be so, in the account, it appeared that these galvanometer sensitivities were defined in opposite ways.

so important as those quoted above, owing to the diminution in the intensity of the light and the correspondingly smaller observed deflections. However, the calculated results are raised to relate to the same standard incident intensity as before and show agreements between the pressure and the energy-density within $+1.1$ and -0.6 per cent respectively.

The above published figures have gained general acceptance as quantitatively confirming, to their stated accuracy, the validity of Maxwell's relation; and for a generation they have been widely quoted as conclusive.

The publication of these figures had, however, two disadvantages. In the first place these figures are not the true results of Nichols and Hull's experiments. It was noticed not only that a wrong value of the mechanical equivalent of heat had been used in the computation of the energy-densities, but also that errors of calculation occurred in the evaluation of the pressures. An erroneous value was taken for the conversion factor F used to reduce the ballistic throws of the vane system to static conditions*. Correct evaluation of Nichols and Hull's results shows the pressure to exceed the energy-density by from 9 to 11 per cent of the latter, the values for full radiation giving the best agreement.

The second disadvantageous effect of the published figures was the creation of a false impression as to the precision attainable, without very great difficulty, in a comparison experiment of this kind. Not only are the pressure and the energy-density, in the case of any laboratory source of light, exceedingly small, but there are so many quantities to be measured and so many corrections to be applied, in addition to possible errors of optical setting, that it is obviously very difficult to obtain final values of pressure and energy-density accurate to less than a few per cent, even if the source be steady and gas action absent. Considering the indirectness of Nichols and Hull's methods, and the small deflections of their torsion balance, the agreement shown in their results, even when correctly calculated, was very satisfactory.

The agreement shown by Nichols and Hull's true results was not definitely improved upon for 30 years. Poynting and Barlow in 1910†, working with blackened and polished surfaces, obtained agreement up to 12 per cent between pressure and energy values, but could not entirely get rid of gas action. Fraulein Golsen‡ showed, in 1924, that radiometer action could be eliminated at a sufficiently high vacuum with metal vanes, and derived agreement varying from $+6$ to -4 per cent. She, however, admits errors of 6 per cent in the measurements. It does not seem that any of the above workers was aware of Nichols and Hull's errors. In the paper by Mary Bell and S. E. Green already referred to, results were given for pressure and energy values which appear to show somewhat better agreement than any hitherto obtained.

* These errors are discussed by Mary Bell and S. E. Green, *Proc. Phys. Soc.* 45, 320 (1933).

† Poynting, *Collected Works*, p. 381 (Cambridge, 1920); *Proc. R. S. A.*, 88, 534 (1910).

‡ *Ann. d. Phys.* 73, 624 (1924).

§ 2. A HISTORICAL STATEMENT

BY G. F. HULL, PH.D.

Received December 28, 1933.

In the March, 1933, number of the *Proceedings of the Physical Society*, Mary Bell and S. E. Green call attention to errors of calculation in the paper on "The Pressure of Radiation" by E. F. Nichols and G. F. Hull, *Proc. Am. Acad.* **38**, 559 (1903). One of these errors, that of the use of the wrong value for the mechanical equivalent of heat, was detected by the writer two or three years after the publication of the article, and in various addresses, notably that before the American Physical Society later referred to, the correct value was given. But the substitution of the correct value did not greatly alter the result, for in the published report the pressure through air as determined by the light-balance was less than that computed from the energy-density by 0.6 per cent. Substituting the correct value made it too large by 1.4 per cent. The discrepancies for red glass and water cell were about 3 and 1.4 per cent, but as the deflections in the three cases were of the order of 100, 60 and 30 chief importance attaches to the through-air readings. The red glass was slightly uneven in quality and variations in its readings might have been due to this fact.

Concerning the factor by which the ballistic throws were reduced to static readings the following considerations may be set forth. First it appeared that the optimum time of exposure would be nearly one quarter of the period. In our case the actual time had to be a whole number of seconds. We chose 6 sec. as this time. It was called a quarter of the period by courtesy. The differential equation was set up and a solution which dispensed with quantities amounting to a fraction of one per cent was obtained.

For example, the equation $\frac{\partial^2 \theta}{\partial t^2} + 2\gamma \frac{\partial \theta}{\partial t} + G\theta = L$ has for its solution*

$$\theta = \frac{L}{G} \left[1 - e^{-\gamma t} \sqrt{(1+x^2)} \cos \left(2\pi \frac{t}{T} - \delta \right) \right],$$

given that $\theta = \partial \theta / \partial t = 0$ when $t = 0$. Here $e^{-\gamma \frac{T}{2}} \cong 0.80$ and $x = rT/2\pi = \tan \delta \cong 0.070$. Hence $\sqrt{(1+x^2)} \cong 1.0024 \cong 1$.

When $\sqrt{(1+x^2)}$ is replaced by 1, δ also drops out of the equation for values of t near zero or $T/2$. But it does not drop out when $t \cong T/4$, a fact which was not evident when we worked out the solution. However, the most serious error was in inadvertently dropping out of the computation the factor $e^{-\gamma t}$ where γ is of the order of 0.02 and t of the order of 2.7 sec., though this factor appears in the solution

* If the light be cut off at time t_1 then thereafter

$$\theta = Ae^{-\gamma t} \cos (2\pi t/T - \alpha),$$

where $A^2 = (L/G)^2 [(1+x^2)(1+e^{-2\gamma t_1}) + 2e^{-\gamma t_1} \sqrt{(1+x^2)} \{x \sin (2\pi t_1/T - \delta) - \cos (2\pi t_1/T - \delta)\}]$

and

$$\tan \alpha = \frac{x + e^{-\gamma t_1} \sqrt{(1+x^2)} \sin (2\pi t_1/T - \delta)}{1 - e^{-\gamma t_1} \sqrt{(1+x^2)} \cos (2\pi t_1/T - \delta)}.$$

Then

$$\theta (\max) = \frac{Ae^{-\gamma t_2}}{\sqrt{(1+x^2)}}, \text{ where } t_2 = T(\alpha - \delta)/2\pi.$$

of the final equation. As a mathematical performance our solution for the general case was very faulty. It was carried out at first for the case in which $\gamma = 0$, in which it was correct. For that case the reduction factor is 1.414. It was then carried out for the first case in hand, in which $e^{-\gamma T/2} = 0.83$ and $T = 23.0$ sec. The exposure time was 6 sec. For that case it is very nearly true that $\theta(t = 6) = L/G$ and the reduction factor is 1.328. The faulty reduction factor 1.357 was worked out very early in the investigation and was used throughout, the thought being that variations in it due to damping or period could be allowed for later.

Through the long series of readings, whenever a ballistic deflection was taken and recorded a static deflection was taken. That is, light was allowed to fall upon the vane until at least twelve turning-points were read. Hence we always had data for determining the value of the pressure without recourse to the ballistic readings. But our light-source was an unsteady arc lamp; the light-balance and the reference galvanometer had different periods and damping coefficients. On the whole we relied on our ballistic readings, since the exposure time and therefore the chance of lamp-variation was twenty-four times as great in the static as in the ballistic measurement. Moreover the gas action in the ballistic method was less.

But our static readings, as also our ballistic, showed that for certain gas pressures radiometric action, as compared with light pressure, had been eliminated to the order of a few per cent.

In their 1900-1901 experiment* Dr Nichols and the writer used a bolometer for measuring the energy of the light-beam. In the data presented in our report we included all the results for air pressures from 96 mm. to 0.06 mm. This was done merely to show that over that large range the ballistic throws were fairly constant and nearly equal to the value demanded by theory. But choosing the region in which the gas action was obviously small, from 37.9 to 33.4 mm., we obtained reduced throws of 21.6, 22.1, 21.1, averaging 21.6 and, applying the correction due to the error in the reducing factor, we obtained the corrected value 23.1 mm.† The pressure corresponding to this deflection is $23.1 \times 4.65 \times 10^{-8}$ or 1.075×10^{-4} dyne/cm². When we reported our results in our first paper we had not measured the reflection coefficients for air-silver and glass-silver. We assumed these to be the same and nearly equal to 0.92. But on application of the correct reflection coefficients 0.92 and 0.77 the pressure should be equal to $\frac{1}{2}(1.92 + 1.77)E$ or 1.85 E .

The energy-density as given in our first report was in error owing to the fact that the resistance of the bolometer as measured, 0.278 Ω ., was too great on account of the silver having been eaten off the leading-in strips‡. A computed value 0.221 Ω . of the resistance was given in our second report. Another computed value, not given there but later worked out, was 0.227 Ω . This was obtained by subtracting from the measured resistance 0.278 Ω . the resistances of the small cylinder-sector strips, each 0.8 mm. long, 5.0 mm. wide, of the thin platinum, for which $\sigma = 0.160$. If the mean resistance is taken as 0.224 Ω ., the pressure of the standard beam computed from

* *Phys. Rev.* 13, 307 (1901).

† For the above pressure-range the period was 24 sec. and the damping ratio 0.790; the correct reducing factor was 1.265.

‡ *Phys. Rev.* 17, 32, 33 (1903).

energy-density should be $1.85 \times 0.224 \times 0.750 \times 10^7$ or 1.030×10^{-4} dyne/cm². After allowance for the fact that the black coating diffusely* reflected 4.5 per cent of the incident radiation, the pressure as computed from the energy-density of the incident beam was 1.075×10^{-4} dyne/cm². The agreement between the two values of the pressure must be regarded as favoured by chance, since the resistance of the bolometer is so critically dependent upon that of the leading-in strips.

When it was stated in our second report that the average error was 6 per cent, the reference was to the results of all the readings for pressures from 96 to 0.06 mm. But when attention is confined to the region given, the average error for the 60 observations (20 for each pressure) was small. There might of course be a large constant error, but inspection of the data shows that the throws were rather free from gas action.

Coming to the data presented in our second and third papers†, there are the following points to be set forth. It was only towards the end of our work that we discovered by our measurements that the reflection coefficient for glass-silver was considerably less than that for air-silver, 0.77 as compared with 0.92. After subtraction of the 4 per cent reflected from the glass surface the absorption on the glass-silver surface was 27 as compared with 8 on the air-silver surfaces. If no gas action whatever was present the light pressures on the two surfaces should have been as 1.77 to 1.92. Since the two deflections were not in that ratio, gas action must have been present.

From table 3 we should then have the relations:

$$1.92L + G = 17.11,$$

$$1.776L - 3.3G = 16.71,$$

where L is the pressure due to incident beam and G the gas action for air-silver surface; this assumes that the gas action is reversed when the vane is reversed.

It results that $1.848L = 16.67$ in place of 16.91, as given in table 3.

Since the period in nine of the observations was nearly 23.75 we find that the correct ratio of ballistic to static is 1.275. After allowance for the 0.8-per-cent correction already applied, the computed pressure is $16.67 \times 1.55/1.265 \times 0.363 \times 10^{-5}$ or 7.40×10^{-5} dyne/cm². The pressure from the corrected energy-density is $7.05 \times 0.98 \times 10^{-5}$ or 6.91×10^{-5} dyne/cm². The discrepancy therefore lies between 6.6 and 7 per cent. The discovery of the error in the ballistic reduction factor has, therefore, brought into agreement the values which were thought to differ by some few per cent, and caused those which were thought to be in close agreement to differ by 6 or 7 per cent.

Lebedew, whose paper on light pressure appeared about the same time as our first paper, rejected, as small, quantities less than 10 per cent and had variations between the two values of light pressure as high as 50 per cent for white light and 80 per cent for blue light. Yet his work is quoted at times as having verified the Maxwell-Bartoli relation.

It might now be enlightening to note the large errors or discrepancies in the

* *Phys. Rev.* 17, 100 (1903).

† *Phys. Rev.* 17, 27, 91, (1903).

measurement of other quantities involving radiation, such as the Stefan-Boltzmann constant σ in the relation $E = \sigma T^4$. The *International Critical Tables* 5, 273 give a list of the most important measurements. These range from 6.5 to 5.3 during the years 1909–1912. Of twenty-one measurements since 1909 only four can claim to have an accuracy of 1 per cent, that by Coblentz who, with all the excellent equipment of the Bureau of Standards at his command and after ten years of continuous labour on this kind of problem, led the way in 1915, and three others of very recent date. To these measurements should be added that of Hoare, whose excellent work was done in 1932. When it is remembered that light-sources and measuring devices have been vastly improved during the past thirty years, it can be seen that the work of Nichols and Hull—involving on the one hand measurements in an absolutely new and perplexing field, the disentangling of light pressure and gas action, and on the other hand measurement of the energy-density of a light-beam in absolute values—established quantitatively the Maxwell-Bartoli relation.

Nichols and Hull made light pressure as capable of exact measurement as other quantities in radiation, and this at ordinary gas pressures. But the writer knew that some gas action was present in their measurements and extended the investigation*. When great care was exercised in making the vane vertical it was shown that the deflection when light fell upon an enclosed black surface was to that for an enclosed silver surface in the ratio 1 : 1.58 for air pressures from 30 mm. to 160 mm. This is the ratio required by the Maxwell-Bartoli relation, as determined by the known reflection coefficients†. Clearly there could be no gas action, even on the black surface, much greater than 1 per cent of the light pressure. Hence on a silvered surface the gas action must have been of the order of $\frac{1}{20}$ per cent. But unfortunately not all the data were published. In Note-Book 10, Third Series, Nov. 29–Dec. 8, 1904, there is a complete series of readings on an air-silver and glass-silver surface, neither surface being enclosed. Here the Maxwell-Bartoli ratio ought to be 1.085. It was found that for air pressures from 20 mm. to 160 mm. the average ratio was 1.08. No gas action as great as 1 per cent could have been present. Consequently it was clear that the chief difficulty in testing the Maxwell-Bartoli relation was that of measuring in absolute units the energy-density of the beam.

Again, before the American Physical Society at the Hanover meeting in 1908‡ the writer demonstrated the effect of a beam of light on a vane of clear glass, on two such vanes, on an enclosed black and on a silvered vane, and showed that the deflections had the ratios 1.0 : 1.7 : 5.6 : 11.5, while the Maxwell-Bartoli relation gave ratios 1 : 1.85 : 5.86 : 11.2; this for an air pressure of about 30 mm. It is beyond doubt that all the American physicists present were convinced that there was no difficulty in getting deflections due to light pressure with practically no gas action present.

Conclusion. When all corrections had been applied, the experiments of Nichols and Hull in 1900–1901 showed that the light pressure computed from the energy-

* *Phys. Rev.* 20, 293 (1922).

† The light source in this case was no longer a sputtering arc lamp but a Nernst filament at a definite voltage.

‡ *Science*, 28, 254 (1906).

density as measured by a bolometer agreed with that determined by the light-balance within 1 per cent. Again, when all corrections have been applied in the later series of 1901-1902, in which a silver disc was used in the measurement of the energy-density, the agreement is within 7 per cent. In view of the very much larger variations in corresponding absolute measurements of radiation which prevailed at that time it can be stated that the experiments of Nichols and Hull verified the theoretical relation of Maxwell and of Bartoli. Further it can be stated that Hull in later work showed that the ratio of the deflections for a black and a silvered surface agreed with the theoretical ratio within 1 per cent; therefore the gas action on the silvered surface could not have been much greater than $\frac{1}{20}$ per cent. To establish an agreement between the two values of light pressure to this degree of accuracy would necessitate measuring the energy-density of a light-beam, with an accuracy which is rather beyond our ability.

§ 3. NOTES ON PROF. HULL'S STATEMENT

BY MARY BELL A.R.C.S., B.Sc., AND S. E. GREEN, PH.D.

Received March 20, 1934.

In our consideration of Nichols and Hull's work we confined our attention to the main experiments, which so far as can be seen from the published papers, were conducted with much greater care and with more attention to experimental detail than any of the earlier ones, and the published results for which have hitherto been generally accepted as conclusive.

Since, however, Dr Hull refers to earlier experiments we will consider *seriatim* the points he has raised. Regarding errors in the constant F , Dr Hull refers to some early experiment in which the period T of the torsion balance was 23.0 sec. and the ratio r^* of successive deflections was 0.83, but with these values we are not concerned as they are not the values of the constants given in the main experiments to which our criticism relates. Further, the calculation of a reduction factor from these values seems to us to be irrelevant, since, as far as can be ascertained, they were not used in any of his published work. Our criticism in connexion with the errors of calculation in the main experiments remains valid, because Nichols and Hull reduced all observations to correspond with a value of 24 sec. exactly for T , and throughout the experiments r was 0.783. In these circumstances the correction factor F required to reduce the vane deflections to static conditions is 1.260 and not 1.357.

As regards the static readings we feel from our own experience that very little reliance can be placed on these at the gas pressures at which Dr Hull worked. He mentions, however, that he relied chiefly on the ballistic observations.

Dr Hull next recalculates the results of a preliminary experiment which was reported much more briefly than the main work. In this early investigation radiation pressure was determined by methods similar to those already described. The

* With the notation employed by Nichols and Hull.

energy-density was found by means of a bolometer. The original published results* were as follows in c.g.s. units:

Total pressure	$1.92E$
1.05×10^{-4}	1.34×10^{-4}

After the publication of the paper in 1901 it was discovered that in dissolving the silver away from the platinum when the bolometer was being made the acid had eaten into the leading-in strips of the bolometer. A direct correction to the resistance of the bolometer was impossible, but a computed correction of the energy values gave the following results, published in 1903†:

Total pressure	$1.92E$
1.05	1.05

Probable errors of about 6 per cent are admitted in these values.

In his present note Dr Hull has made five further corrections of which (i) and (ii) relate to the pressure and (iii), (iv) and (v) to the energy-density. (i) The results for the range of gas pressures 37.9 mm. to 33.4 mm. (at which gas action appeared to be a minimum) have now been selected, the complete range of pressures having originally been from 0.02 mm. to 96 mm. This reduces the mean deflection from 22.5 mm. to 21.6 mm., a difference of 5 per cent. (ii) Revaluating his correction factor F , and avoiding errors in his calculation pointed out by us, Dr Hull has now used the value 1.265 instead of 1.357. (iii) Instead of the original assumed value of 92 per cent for the mean reflection coefficient of the vanes, a new value 85 per cent, obtained by direct experiment on silvered surfaces two years later, has now been used. (iv) A further correction to the bolometer resistance has been introduced. (v) Allowance has been made for the light diffusively reflected from the blackened surface of the bolometer.

The new results after all these corrections have been applied are

Total pressure	$1.85E$
1.075	1.075

Dr Hull states that the final agreement was fortuitous, and this is obviously so since, all other corrections apart, the new corrections to the bolometer resistance (admitted by Dr Hull to be a very critical factor) bring into agreement pressure and energy values which otherwise would differ by 20 per cent.

We may mention that since the value of r was not given in the published papers, we were not able to check the value of the correction factor F for the preliminary experiments, as we had done in the case of the main work.

With reference to the main experiments outlined in the first part of this paper,

* *Phys. Rev.* 13, 318 (1901).

† *Phys. Rev.* 17, 33 (1903). Only significant figures have here been retained.

Dr Hull, who originally regarded gas action as negligible, has now recalculated the results on the basis that some gas action was present. This correction seems to us to be rather unreliable for two reasons. Firstly the correction applied only amounts to 0.2 mm. in a deflection of 16 mm., whereas during the experiment the zero wandered by more than 1 mm. Certainly the zero was always checked, but to apply the correction at all appears to be unduly straining the accuracy of the observations. Secondly, if his assumptions regarding gas action were correct, the ratio of any pair of observed deflections should be greater than $1.92/1.77$. Out of eleven pairs of observations given by Nichols and Hull, in one case the deflections are equal and in four others the ratio is actually less than unity. Thus in these cases the gas action was in the contrary direction to that which Dr Hull postulated from the final mean values. If there had been a definite gas action it should certainly have acted in the same direction in every case. We feel also, from our own experience, that at the relatively high gas pressure used in his torsion chamber it was not possible to obtain gas effects constant enough to be satisfactorily eliminated by calculation. However, we can only express a tentative opinion on this point since the arrangement of our apparatus was different from that of Nichols and Hull.

Incidentally, in the calculation of the final value of the pressure it appears to us that the figure in the denominator should be the correct factor 1.260 and not 1.265 as the deflection 16.67 relates to a balance period of 24 sec. exactly.

We are glad to have the ambiguity in Nichols and Hull's use of their galvanometers removed and to learn that our inference was correct, namely, that galvanometer-sensitivity had been defined directly in the case of G_2 and inversely in the case of G_1 . The sensitiveness was taken for the former instrument as proportional to the deflection for a given voltage across the terminals, and for the latter as proportional to the voltage producing unit deflection.

The correction for gas action now introduced by Dr Hull, even if justified, does not greatly affect the divergence between the pressure and energy-density results, which we have shown in the case of full radiation to be 9 per cent of the latter.* The errors we pointed out were merely of calculation, and do not detract from the experimental ingenuity with which Nichols and Hull conducted their classical investigation. We do, however, claim for our own methods the great advantages of simplicity and directness, with the consequent possibility of avoiding the majority of the complicated corrections inherent to the work of Nichols and Hull. In particular we may mention that modern research had made available to us a steady source of light and a ready means of obtaining a high vacuum, and further had provided a simple and accurate method of determining the energy of the incident beam. Our work has shewn that the high-vacuum method with the use of metal vanes is capable of disentangling radiation pressure from gas action with much greater certainty than any other method. With the advantages enumerated we naturally were able to obtain somewhat better agreement between pressure and energy values than could have been obtained from the unavoidably circuitous methods adopted by Nichols and Hull.

* See p. 596.

THE ACTION OF ALTERNATING AND MOVING MAGNETIC FIELDS UPON PARTICLES OF MAGNETIC SUBSTANCES

BY H. STAFFORD HATFIELD, PH.D.

Communicated by Prof. E. N. da C. Andrade, March 7, 1934. Read June 1, 1934.

ABSTRACT. The paper offers an explanation of the translatory movement observed by Mr W. M. Mordey in magnetic particles subjected to a multi-phase alternating field.

SOME years ago Mr W. M. Mordey* discovered some striking phenomena exhibited by magnetic particles when exposed to single and multi-phase magnetic alternating fields. He found that particles of various magnetic substances, such as magnetite, specular haematite, and pyrrhotite ($Fe_n S_{n+1}$), when strewn upon a surface situated over one pole of a vertical single-phase alternating bar magnet, were in part attracted to the region over the pole and in part repelled away from it, forming a circular halo concentric with the pole. He also found that if the single-phase magnet were replaced by a row of poles excited alternately by two-phase current, the particles travelled in a direction along the line joining the poles.

A multi-phase magnet of this type is equivalent to a procession of alternate north and south poles travelling with a speed depending upon the periodicity of the supply. The particles of magnetic material travel in a direction opposite to that in which the field is travelling, although Mr Mordey does not seem to have stated this fact. They travel, in fact, in the opposite direction to that in which the edge of a sheet of metal is dragged by the induced eddy currents, as in the ordinary house-service alternating-current meter, the armature of which is an aluminium disc acted upon by a two-phase magnet.

No investigation leading to a clear physical explanation of these phenomena seems to have been published. Mr Mordey suggested that hysteresis might be concerned, and even that some minerals might be diamagnetic to alternating current, though paramagnetic to direct fields. The experiments described in the present paper were carried out with a view to finding some more satisfactory explanation. The frequency of the alternating current used was 150 c./sec. A microphone transformer served as a single-phase bar magnet, and a permanent magnet was arranged to rotate about an axis parallel to, and midway between, its limbs, and so to provide a moving field. A four-pole two-phase magnet was made of stalloy stampings, one pair of windings being connected through a non-inductive resistance, and the other through a condenser, to the alternating supply. The magnetic powders employed

* W. M. Mordey, *Phys. Soc. Proc.* 40, 338 (1928).

were iron filings, magnetite, pyrrhotite, tungsten steel filings, and $\frac{1}{16}$ -in. steel bearing balls. Globules of magnetite were also made, by fusion with an oxy-gas flame.

Mr Mordey's phenomena were easily reproduced, the rotating magnet giving results similar to those obtained with the two-phase magnet. It was found that when either of them was below the surface on which the particles rested, as in Mordey's arrangement, motion took place in the opposite direction to that of the field; when the magnet was above the surface, travel took place *with* the field. If, however, the two-phase magnet was brought too near to the surface, the particles ceased to travel and were attracted to the poles.

When the magnetic matter, either in the form of lump or of powder, was attached by adhesive to one arm of a sensitive torsion balance, no anomalous re-

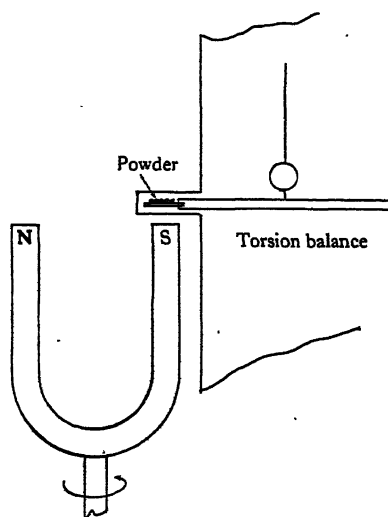


Figure 1.

pulsive or translatory force was observed in the field of the rotating permanent magnet, arranged as in figure 1, or in those of the single-phase and two-phase magnets. The only force observed was attraction in the direction of maximum increase of field-strength. If the arm of the torsion balance pointed towards the axis of rotation of the magnet, no deflection occurred. Yet loose particles resting upon a surface in the same position relatively to the magnet are driven, as if by a blast of air, in a direction opposite to the motion of the magnet poles. On the other hand, particles allowed to fall freely through the moving field are not deflected either in, or against, the direction of its motion. This indicates clearly that the action observed upon particles lying loose upon a surface is due to reaction between them and the surface.

A slip of mica coated with magnetic powder stuck on with an adhesive, and pivoted so as to turn in a horizontal plane about the same axis as the magnet, rotated in the same direction as the latter. This is the well-known hysteresis effect, commonly exhibited in the Ewing hysteresis tester. Mr Mordey refers to similar

arrangements in his paper, but they afford no explanation of the motion of free particles, which is in the opposite direction. Particles strewn upon a surface situated over the rotating magnet swirl round in the direction opposite to its rotation, being also drawn towards the axis, where they form a kind of whirlpool.

The single-phase magnet was found to repel the particles when below the surface, as in Mordey's arrangement, but to attract them when above it.

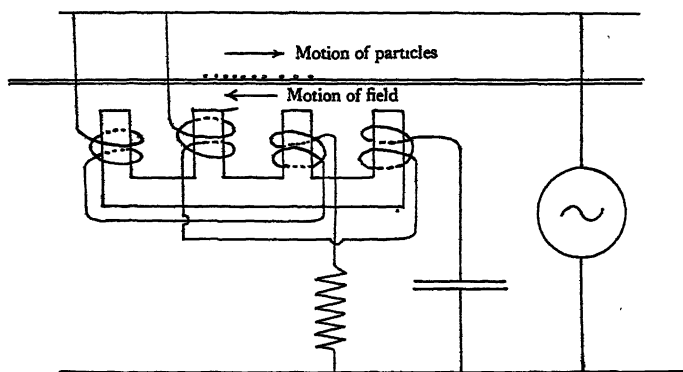


Figure 2.

The clue to an explanation was given by the fact that magnetite particles could be rendered almost inactive by exposing them to a strong alternating field for a little while, and restored to activity by exposing them to a unidirectional field. The first

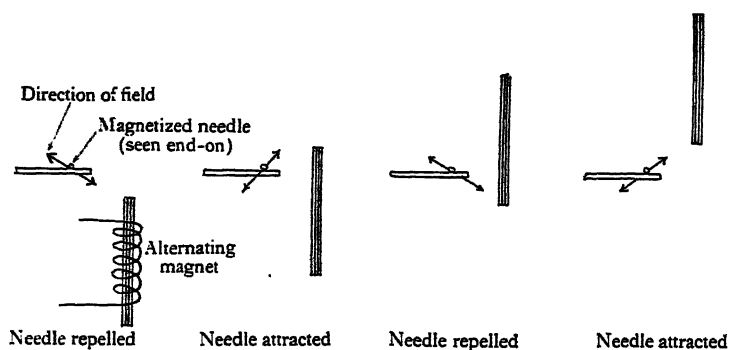


Figure 3.

process destroys their permanent magnetism, the second restores it. The mechanism of attraction and repulsion is easily demonstrated by means of the experiments shown in figures 3 and 4. A short piece of magnetized sewing-needle rests upon a horizontal glass plate, the length of the needle being at right angles to the line joining its centre to the axis of the bar magnet fed with alternating current. In figure 3 the needle is seen end-on.

We find that the needle moves towards or away from the magnet according to the level of the latter. If, as in figure 4, we arrange that one pole of a magnetized needle suspended by a thread shall rest upon the edge of a glass plate and if we act upon it

with the magnet in the various relative positions shown in figure 3, we find that the single pole now moves in the same sense as the fragment in figure 3.

The explanation which suggests itself is as follows. During one half of a cycle, the field is acting upon a pole with, say, an oblique downward force. The horizontal component of this force cannot move the particle along the surface, for it is opposed by friction under the combined weight of the particle and the vertical downward component of the magnetic force. During the other half of the cycle the vertical component tends to lift the pole; hence the horizontal component can act, and the pole moves. The fragment of needle resting with both its poles upon the glass progresses by stepping out, as it were, with each pole alternately. It owes its motion to the fact that either pole can only move when the force on it has a component in the upward direction.

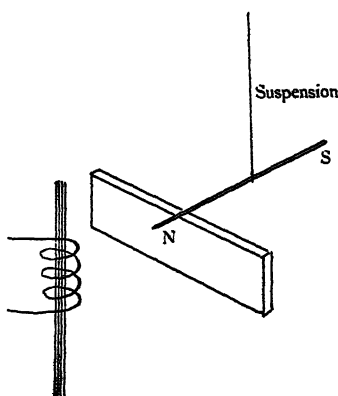


Figure 4.

The above explanation is confirmed by the fact that spherical particles, such as steel balls or globules of magnetite, are entirely inactive even when strongly magnetized. The poles are very close together, and the forces on them are almost exactly equal and opposite in any direction. The only effect they can have is to cause the sphere to oscillate slightly from side to side but not to progress, since it touches the surface only at one point.

The action of moving fields can be explained on similar lines. At any point past which a succession of field-magnet poles is travelling, figure 5, the direction of the field they produce at a given point undergoes complete revolutions; in the figure, the field poles are imagined as travelling to the right, and the field at any point on the surface thus rotates counter-clockwise. Its intensity in each direction is symmetrical on either side of the vertical. During one half of a cycle it possesses an upward or lifting component for one or other pole (N in the figure) of a particle resting on the surface; this component reaches a maximum half-way through the half-cycle. The direction of the horizontal component changes from urging the particle pole in the direction of travel of the field poles, through zero, to urging it in the opposite direction. But it can only act effectively after the lifting component has lifted the particle. Since the particle takes time to rise and fall, the horizontal component

urging it against the direction of travel of the field poles is effective for a longer time than the component in the opposite direction; the particle leaves the surface in the upward force at a point making a certain angle with the vertical, but does not return to the surface until the force makes a greater angle on the other side of the vertical. This is the clue to the phenomenon, as may be seen by studying the horizontal and vertical components of the force exerted on a north pole in different positions, as shown in figure 5.

It should be noted that, in this case, the revolution of the field must produce a torque on the particle, due to hysteresis, and tending to roll it along the surface in the observed direction. This, however, is very weak, for it is ineffective to produce motion in the very case where circumstances are most favourable to its action, namely that of spherical particles.

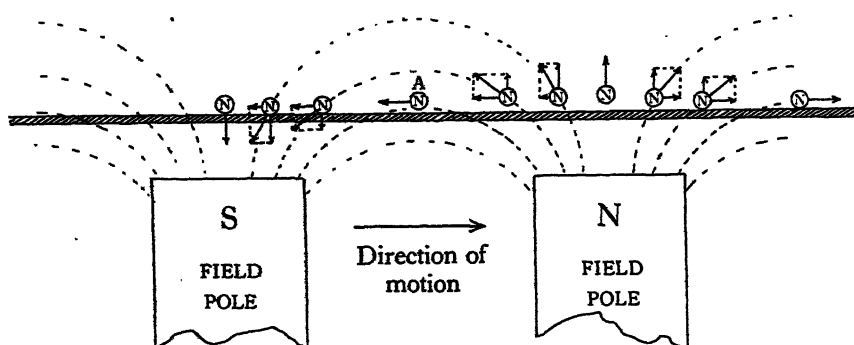


Figure 5.

As the phenomenon depends upon the particles being lifted by a field rapidly reversing in direction, it is clear that they must be small to respond to a high frequency. At 150 c./sec., particles of larger size than 60 mesh (say, 0.3 mm. in diameter) are very sluggish, and those over 20 mesh (say, 0.9 mm. in diameter) hardly move. There is no action, according to the above hypothesis, upon a particle the magnetic axis of which lies in the direction of the field; this is easily demonstrated with the magnetized needle. Hence the particles need to be small to be flung about by the field; they then travel when they happen to fall aright. The extremely lively motions of some of the particles are very striking; they strongly suggest gnats. If these lively particles are isolated they do not seem to differ in any way from the rest. Probably they are of such a size as easily to revolve synchronously with the field when in the air.

It is possible that a study of the demagnetization of magnetite by alternating current would have interesting results. It takes time of the order of seconds, and the material thus treated regains its activity spontaneously with time.

This work was carried out in the Physics Department of University College, London, under a Fellowship grant from the Leverhulme Trustees, to whom I beg to express my thanks, which are also due to Professor E. N. da C. Andrade for the kind and helpful interest which he has taken in the investigation.

NOTE ADDED JUNE 12, 1934

Since the above paper was read my attention has been drawn to a hypothesis put forward by Prof. J. A. Fleming in his book *Scientific Research and Electrical Engineering*, in which he attempts to explain the Mordey effect. He assumes that a particle of a ferromagnetic substance exhibiting hysteresis, when situated in the field of an alternating magnet may experience a repulsive force, owing, as he says, to the fact that "the induced pole in the particle nearest to the magnet will always be of similar polarity." Again: "The particles possess ferromagnetic permeability, in virtue of which they tend to move from weak to strong places in the magnetic field. But they also possess magnetic hysteresis, and in consequence there is a dissipation of energy. The particle, therefore, tends to move from strong to weak places in the field to make this dissipation a minimum, and its actual position depends upon the relative magnitude of the two forces."

It would appear that the repulsive forces considered by Prof. Fleming, if they exist, cannot possibly account for the major portion of the effect, since my torsion balance was amply sensitive enough to detect forces of the necessary magnitude. Furthermore, the fact that the Mordey effects are greatly increased by first exposing the particles to a unidirectional field, and so permanently magnetizing them, seems to contradict the assumptions made by Prof. Fleming.

DISCUSSION

Prof. S. CHAPMAN said that he had investigated Mr Mordey's proposed explanation of the phenomenon under discussion but had found that it yielded results of the wrong magnitude. The author was the first to hit upon the true explanation.

Mr S. N. RAY. The author is the first to have provided a physical explanation of the Mordey effect. This effect is being studied by me at the Sir John Cass Technical Institute under Dr D. Owen, but owing to the work being only part-time the progress has been slow. Specular haematite (Elba) and pyrrhotite (Norway) have been studied with an electromagnet having a stalloy core, and alternating current at 100 c./s. With a delicate torsion balance no anomalous diamagnetic repulsion has been observed either in lumps or with masses of powdered material. The author's explanation of the change of repulsion into attraction, as the level of the surface carrying the powder is lowered below that of the pole-faces, is a valuable contribution to our knowledge of this phenomenon.

Owing to the sluggishness and erratic movement of the particles with a rapidly alternating field it has been found convenient to use direct current, very slowly reversed with a commutator, for the electromagnet. With such a supply a microscopic study of the particles shows motion resembling a somersault or a forward jump rather than the stepping out of the fragment of needle described by the author. Again, the repulsion effect can still be produced when the active particles are enclosed in spheres of paraffin wax.

These two observations do not fit in with the author's account of the process but can be explained from the known magnetic properties of haematite*, namely, ferromagnetism with large hysteresis along the principal axis and different degrees of paramagnetism along the remaining axes. Such a crystal at rest in a unidirectional magnetic field will be subjected to a couple when the field is reversed, owing to the resultant magnetic intensity not being turned through 180° at the same time. It may well be, therefore, that Mr Mordey's opinion that the explanation is somehow bound up with the large hysteresis is not entirely without foundation.

It would be interesting to learn if the author has succeeded in producing the drift with particles of materials of high coercive force, such as cobalt steel or tungsten steel. If they are first magnetized to saturation by a unidirectional field at right angles to the alternating field and then subjected to the latter, the particles should step away from the pole as described by the author.

AUTHOR'S reply. As I mentioned in the paper, I have observed the stepping-out motion in weak fields, but in strong ones the same forces are sufficient to cause the particles to be flung about quite violently.

I am not very clear as to Mr Ray's remarks on haematite. His observation that particles enclosed in wax spheres are repelled is interesting, and seems to contradict my observation that spherical particles will not move. It should be noted that the essential difference between the hysteresis theory and my own permanent-magnetism theory lies in the fact that in the first case the field is supposed to reverse the magnetization of the particles at each alternation, in the second not. The fact that particles lose their activity after long exposure to an alternating field and regain it after exposure to a unidirectional field seems to me decisive in favour of the second view.

As I explained in the paper, hard steel balls are the most favourable objects for the exercise of hysteresis effects, and yet neither they nor magnetite spheres are affected in the slightest. Cobalt-, tungsten-, and carbon-steel filings move vigorously.

The torsion balance excludes the theory given by Prof. Fleming. The particle needs the surface in order to move. Hysteresis could only act by rolling the particle along the surface; the tendency to roll is there but is too weak to be effective even in the most favourable case. We must conclude that the particle needs to retain a permanent polarity, which suffices to explain its motion.

* Townsend Smith, *Phys. Rev.* 8, 721 (1916), 15, 345 (1920).

THE APPLICATION OF THE THEORY OF THE TRANSMITTING ECHELON TO THE EXPLANATION OF TALBOT'S AND POWELL'S BANDS

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ABSTRACT. On the basis of the theory of the transmitting echelon, the formation and the asymmetrical character of Talbot's bands, which are produced when a plate and aperture are placed in certain positions in the beam of a prism spectroscope, are explained analytically and represented diagrammatically. The effects of variation of aperture-width, plate-thickness and inclination of the echelon to the beam are considered. It is contended, in contradiction to A. W. Porter's conclusion, that perfect blackness of the dark bands is approached as the thickness of the plate increases. The appearance of bands when the plate and aperture are placed in front of the spectroscope slit is discussed. A direct diagrammatic representation is given of the formation of bands as photographed by A. C. G. Beach when prism and echelon dispersions are at right-angles. The fact, reported by N. K. Sethi, that in the case of Powell's bands the asymmetry can be reversed by suitable choice of liquid is accounted for, and the criterion for reversal is shown to be equivalent to that stated by Sethi.

§ 1. HISTORICAL REVIEW

THE interference bands observed in a continuous spectrum produced by a prism spectroscope when a thin film of glass or mica is placed in one of three positions across a portion of the beam were first described by Talbot* in 1837. The most remarkable feature of these bands is that whereas they appear when the film is placed in the beam between the collimator and telescope, so that the intercepted part of the beam traverses the thicker part of the prism, no bands can be observed when the film is placed towards the base of the prism so that the unintercepted part of the beam traverses the thinner part of the prism. Again, the bands can be seen if the film intercepts the beam emerging from the eyepiece on the side towards the violet part of the spectrum but not if the other side of the beam is intercepted. The explanation of the bands as given by Talbot was incomplete in that this asymmetry in the method of production of the bands was not accounted for.

A similar system of bands was described by Powell† in 1848. Into a hollow glass spectroscope prism containing a highly refractive liquid is inserted a plate of glass with its edge parallel to the refracting edge of the prism to intercept a portion

* H. F. Talbot, *Phil. Mag.* 72, 364 (1837).

† B. Powell, *Phil. Trans.* 138, 213 (1848).

of the beam from the collimator. The continuous spectrum produced by the prism is crossed by bands if the liquid has a smaller refractive index than the glass plate and if the plate is in the thinner part of the prism, whereas if the index of the liquid is greater than that of the plate the latter must be moved to the thicker part of the prism.

The complete analytical investigation of Talbot's bands was accomplished by Airy* and later by Stokes†. Their explanations of the asymmetry involve long and complicated mathematical processes and in consequence the physical aspects of the problem are somewhat obscured.

A simple explanation of the asymmetry based on the ether pulse theory of light was given by Schuster‡. The success of this theory in its application to Talbot's bands gave it strong support when it was a subject of much speculation and controversy.

The suggestion that Talbot's bands might be explained by regarding the film and aperture used for their production as an echelon of two elements was first made by Wood§. Porter||, following this method of treatment, has given an incomplete and very rough theory of the bands in which the case of almost normal incidence only is considered, and it is concluded that the blackness of the dark bands should increase with diminishing thickness of plate, a result which, as will appear later, a more exact theory shows to be erroneous. For teaching purposes and for experimental application of the bands the author has found these and other accounts existing in the literature of the subject to be inadequate. The theory to be developed, in addition to accounting for Talbot's and Powell's bands and their asymmetrical character, deals with the effect of variation of aperture-width, thickness of plate and angle of incidence of the beam on the echelon. The fact reported by Sethi¶ that in the case of Powell's bands the asymmetry can be reversed by suitable choice of liquid is accounted for, and the criterion for reversal is shown to be equivalent to that stated by Sethi.

§ 2. TALBOT'S BANDS

Normal incidence. Consider the diffraction pattern due to normally incident light of wave-length λ passing through a narrow aperture of uniform width $2s$. The intensity of the beam diffracted in a direction inclined at an angle α to the normal is

$$I_{\alpha} = A^2 \frac{\sin^2 X}{X^2} \quad \dots\dots(1).$$

where A is a constant depending on the intensity of the incident beam, and X is half the phase-difference between extreme rays of the diffracted beam and $= \lambda^{-1} \pi 2s \sin \alpha$. There is a central maximum given by $X = 0$, i.e. $\alpha = 0$, and other

* G. B. Airy, *Phil. Trans.* 130, 225 (1840) and 131, 1 (1841).

† G. G. Stokes, *Phil. Trans.* 138, 227 (1848).

‡ A. Schuster, *Phil. Mag.* 7, 1 (1904).

§ R. W. Wood, *Phil. Mag.* 18, 758 (1909), and *Physical Optics*, p. 254 (1921).

|| T. Preston, *Theory of Light*, p. 320. (Edited by A. W. Porter, 1928.)

¶ N. K. Sethi, *Phys. Rev.* 16, 519 (1920).

fainter maxima are given by $X = \pm \frac{1}{2} (2m + 1) \pi$; $m = 0.93, 1.96, 2.97, 3.98$, etc. The minima of zero intensity on each side of the central maximum are given by $X = \pm m\pi$, $m = 1, 2, 3$, etc., i.e. $\alpha = \pm \sin^{-1}(m\lambda/2s)$. If one-half of the aperture be covered by a transparent plate of uniform thickness the intensity-distribution is considerably modified, being given as in the case of a two-slit grating by

$$I_{\alpha} = \left(\frac{A \sin X}{X} \right)^2 \left(\frac{\sin 2Y}{\sin Y} \right)^2 \quad \dots\dots(2).$$

The first factor is the effect due to a single aperture, with X now equal to $\lambda^{-1}\pi s \sin \alpha$. The second factor represents the effect of interference between corresponding rays from the two elements. Y is half the phase-difference between such rays. If t is the thickness of the plate and μ its refractive index relative to air for

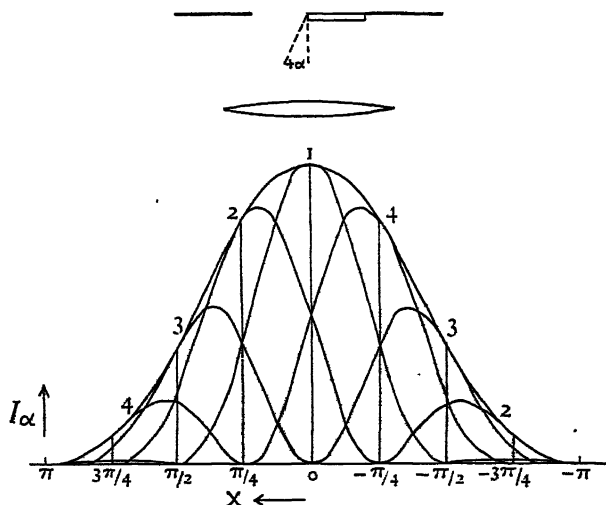


Figure 1. Progression of maxima of a given order with increase of wave-length.

light of wave-length λ , $Y = \pi\lambda^{-1} (\mu t + s \sin \alpha - t \cos \alpha)$. The angle of diffraction α is taken to be positive measured from the normal on the side opposite to the plate. If α is small we may write approximately

$$X = \pi s \alpha / \lambda, \quad Y = \lambda^{-1} \pi (\mu - 1) t + X \quad \dots\dots(3).$$

The second factor has maxima when $Y = m\pi$, $m = 0, 1, 2, 3$, etc., and is zero when $Y = \frac{1}{2}k\pi$, k being an odd integer.

Equation (2) may be re-written

$$I_{\alpha} = 4A^2 \cdot \frac{\sin^2 X}{X^2} \cdot \cos^2 Y \quad \dots\dots(4).$$

The maximum value of the $\cos^2 Y$ is unity, so that with fourfold increase of intensity the single-aperture curve envelopes the interference maxima. If α is small then from the approximate form of (3) the angular separation of successive maxima of $\cos^2 Y$ = the angular separation of successive minima of $\cos^2 Y = \lambda/s$; the separation between a maximum and either of the next minima is $\lambda/2s$. Figure 1 shows several resultant I_{α} curves for light of slightly different wave-lengths

enveloped by a $X^{-2} \sin^2 X$ curve. In general for a given λ there are two maxima of I_α , but when maxima of I_α and $X^{-2} \sin^2 X$ coincide there is only one, the consecutive I_α maxima coinciding with zero minima of $X^{-2} \sin^2 X$. Thus the spectra may be of double- or single-order type. The separation of double-order I_α maxima is less than that of maxima of $\cos^2 Y$ and is variable, while the separation of double-order minima is constant and equal to the separation of the single-aperture maximum and either of its adjacent minima. Since the spread of any subsidiary-maximum curve of $X^{-2} \sin^2 X$ is half that of the central-maximum curve, there can be only one maximum of I_α within it for light of a given wave-length. If the wave-length is such that the central maximum of $X^{-2} \sin^2 X$ and an I_α maximum coincide, all light of this wave-length is concentrated in that order, for the corresponding maxima of I_α coincide with zero minima between subsidiary maxima of $X^{-2} \sin^2 X$.

For light of a given wave-length, decrease in the thickness of the plate will cause the maximum of any particular order to move in the plate-to-aperture direction, i.e. from right to left in figure 1. The direction of progression of the maxima is the same if the plate-thickness is constant and the wave-length of the incident light is continuously increased. In this latter case we see that $d\alpha/d\lambda$ is positive for a fixed value of the order m ; or $dm/d\lambda$ is negative in a direction α , figure 2*a*.

Suppose that $Y = m\pi$ for light of wave-length λ_1 in the direction $\alpha = 0$; then if light of this wave-length is incident on the echelon the spectrum will be a single-order one and the corresponding retardation $(\mu - 1)t = m\lambda_1$. If light of slightly shorter and longer wave-lengths $\lambda - d\lambda_\alpha$, $\lambda + d\lambda_\alpha$ also is incident, the component intensity distributions will be as indicated in figure 2*a*, the m th-order spectrum of the shorter wave-length being on the plate side of the single-order maximum for λ_1 while the m th-order spectrum of the longer wave-length is on the aperture side. We neglect here the slight change in the spread of the single-aperture curve corresponding to $d\lambda$ and also the effect of the accompanying single-aperture maxima, which relatively are very faint.

Now suppose the aperture and plate to be placed between the collimator and prism of a spectroscope, so that light from the centre of the slit forms a normally incident parallel beam. Let the aperture be on the base side of the prism. Under these conditions the dispersions of echelon and prism, $d\alpha/d\lambda$ and $d\phi/d\lambda$, are opposed. Suppose that they are numerically equal: then the component intensity curves are as shown in figure 2*b*. Relative to the single aperture curve for λ_1 those for $\lambda_1 - d\lambda_\alpha$ and $\lambda_1 + d\lambda_\alpha$ are displaced, the former towards the base of the prism, the latter away from it. The m th-order spectra of $\lambda_1 - d\lambda_\alpha$ and $\lambda_1 + d\lambda_\alpha$ approach to coincide with each other and with the m th order of λ_1 . The $(m + 1)$ th order of $\lambda_1 - d\lambda_\alpha$ and the $(m - 1)$ th of $\lambda_1 + d\lambda_\alpha$ are symmetrical in intensity and position with respect to the m th order maxima, the former appearing on the base side, the latter on the edge side, while each is separated from the m th maxima by slightly less than half the distance between single-aperture minima.

The effect of increasing $\lambda_1 + d\lambda_\alpha$ and decreasing $\lambda_1 - d\lambda_\alpha$ by equal amounts is

illustrated in figure 2 *c, d, e*. In all cases *m*th, (*m* + 1)th and (*m* - 1)th orders coincide and the intermediate zero minima remain unchanged in position. In figure 2 *e* the *m*th orders of $\lambda_1 + d\lambda_a$ and $\lambda_1 - d\lambda_a$ are of zero intensity while the (*m* + 1)th of $\lambda_1 - d\lambda_a$ and the (*m* - 1)th of $\lambda_1 + d\lambda_a$ have the greatest intensities

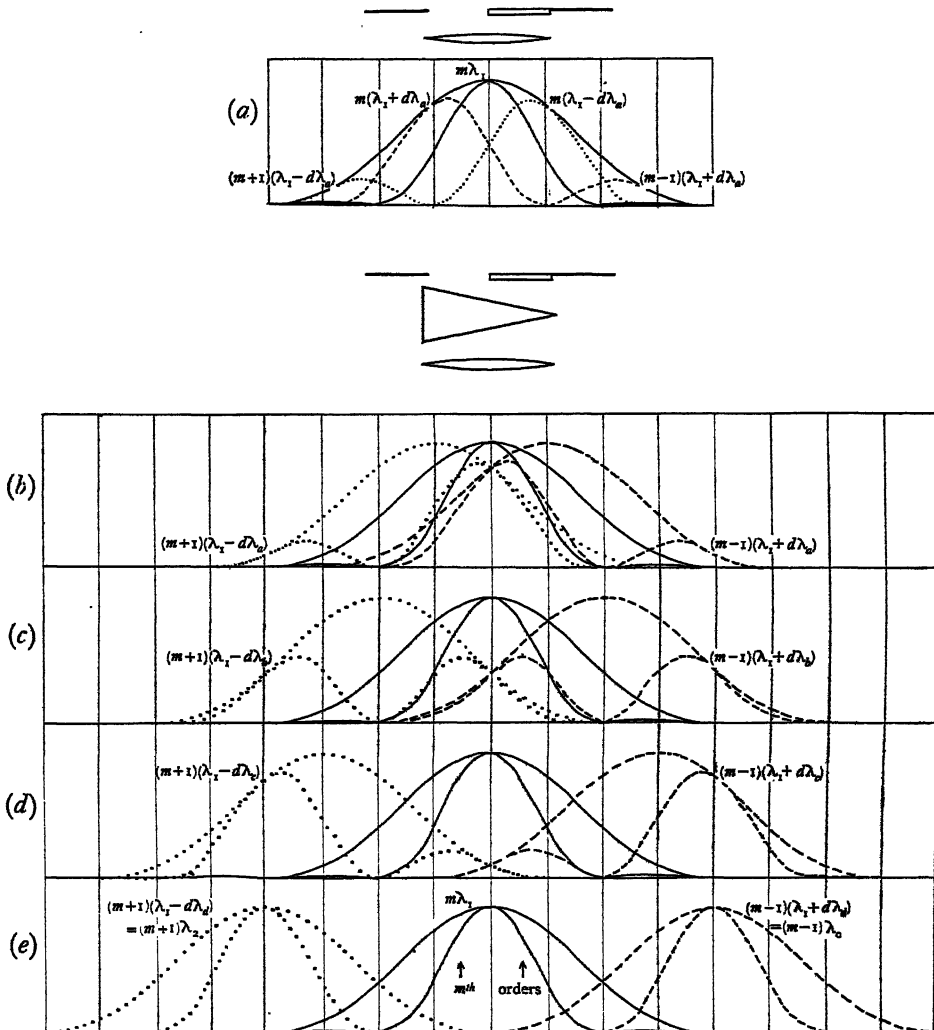


Figure 2. (*a*), intensity-distribution of λ_1 , $\lambda_1 + d\lambda_a$, $\lambda_1 - d\lambda_a$ without prism; (*b, c, d, e*), intensity-distributions of light between λ_0 and λ_2 with prism. $\lambda_0 > \lambda_1 > \lambda_2$, $d\lambda_a < d\lambda_b < d\lambda_c < d\lambda_d$.

possible, coinciding with single-aperture maxima. Writing $d\lambda_a = \lambda_1 - \lambda_2 = \lambda_0 - \lambda_1$ and neglecting $d\mu/d\lambda$ we have thus consecutive Talbot bright bands in the spectrum of light between λ_0 and λ_2 at wave-lengths λ_0 , λ_1 , λ_2 such that

$$(m - 1) \lambda_0 = m\lambda_1 = (m + 1) \lambda_2.$$

The separation of these maxima is the same as that between a single-aperture

maximum and the associated first minimum in this region. Talbot dark bands occur at wave-lengths $\lambda_1 + d\lambda_b$ and $\lambda_1 - d\lambda_b$, figure 2c, and for them

$$(m - \frac{1}{2})(\lambda_1 + d\lambda_b) = (m + \frac{1}{2})(\lambda_1 - d\lambda_b).$$

If ${}_0\lambda_1, {}_1\lambda_2, {}_2\lambda_3$ denote wave-lengths for which consecutive dark bands occur,

$$(m - \frac{1}{2}){}_0\lambda_1 = (m + \frac{1}{2}){}_1\lambda_2 = (m + \frac{3}{2}){}_2\lambda_3.$$

Now consider the case in which the plate is on the prism-base side of the aperture. Without the prism the m th order of $(\lambda_1 + d\lambda_a)$ is to the right of the m th order of λ_1 and the m th of $(\lambda_1 - d\lambda_a)$ is to the left, figure 3a. Let these spectra be dispersed by means of the prism, still placed with its base to the left. Figures 3b, c, d show an increasing separation of the m th-order spectra of $\lambda_1 + d\lambda$ and $\lambda_1 - d\lambda$ as $d\lambda$ is gradually increased. At the same time the $(m - 1)$ th and $(m + 1)$ th spectra move in opposite directions, cross each other and attain their maximum intensities in the same positions as in figure 2e. It is to be observed that whereas figures 3c, e are identical with figures 2c, e, as regards intensity-distribution, figures 3b, d and 2b, d are quite different, and because of this difference we should obtain, if figures b, c, d, e were superposed in the two cases, intense bright bands separated by zero minima in one case and an almost uniformly intense continuous spectrum in the other. If the illumination is now perfectly continuous the effects are enhanced and we get in one case Talbot's bands and in the other a continuous spectrum in which there is no trace of bands whatever.

It is to be observed that all light of any one of the wave-lengths $\lambda_0, \lambda_1, \lambda_2$, etc. satisfying the equations $(m - 1)\lambda_0 = (\mu_0 - 1)z$, $m\lambda_1 = (\mu_1 - 1)z$, etc. is concentrated in the corresponding single order. Other orders, for example $(m - 2)$, $(m - 1)$, $(m + 1)$, and $(m + 2)$ of λ_1 , coincide with single-aperture zero minima. Spectra outside the range of the single-aperture central maximum are of light intermediate in wave-length between $\lambda_0, \lambda_1, \lambda_2$, etc. Within the range of any single-aperture subsidiary maximum, there can be only one double-aperture maximum of light of any intermediate wave-length, for the separation of double-aperture minima is the same as that of minima between subsidiary single-aperture maxima. Hence the above argument concerning juxtaposition of light of the same orders when echelon and prism dispersions are equal remains valid when maxima outside the range of the central single-aperture maximum are considered.

The explanation of Talbot's bands given by Walker* and to which reference has been made recently by Milne† must be regarded as incomplete and unsatisfactory since no account is taken of the production of double-order spectra by the plate and aperture.

Incidence not normal. The effect of rotating the echelon about a vertical axis when it is so placed as to produce bands is to alter the values of X and Y , and a shift of the bands across the spectrum results. The appearance or non-appearance of the bands is not dependent on the angle of incidence of the beam.

* J. Walker, *Phil. Mag.* 11, 531 (1906).

† J. R. Milne, Discussion on paper by A. C. G. Beach, *Proc. Phys. Soc.* 45, 474 (1933).

If the echelon is placed between the prism and telescope the above method of explanation still applies. In the former case the angle of incidence on the echelon is the same for all wave-lengths but the angle of incidence on the prism depends on the wave-length, while in the latter case the angle of incidence on the prism is the same for all wave-lengths but that on the echelon varies with wave-length.

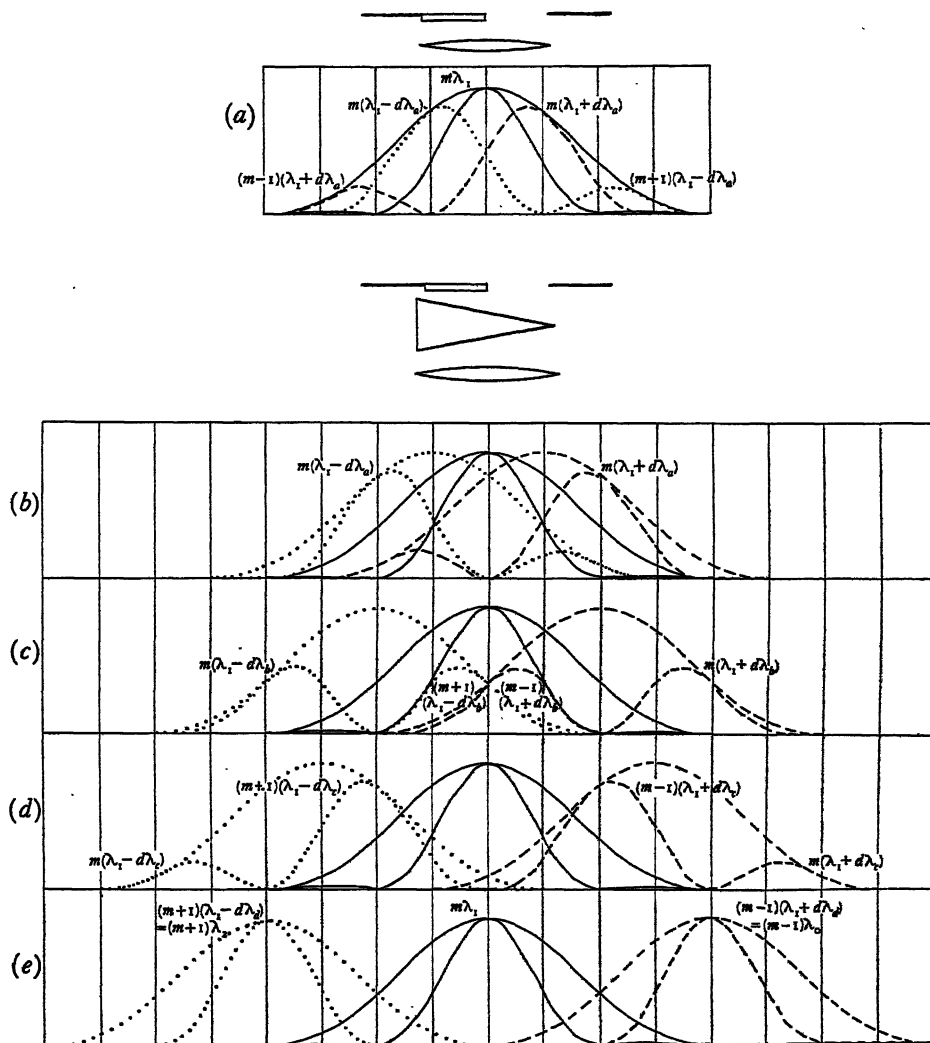


Figure 3. Intensity-distributions corresponding to figure 2 but with echelon reversed.

The case of the echelon between prism and telescope is the one dealt with by Porter*, to whose treatment reference has already been made. We proceed to the analytical deduction of the condition to be satisfied if the bands are to appear.

* Loc. cit.

The conditions obtaining involve the theory of the tilted echelon, which has been treated very fully by Galitzin* and presented in a simplified form by Williams†.

Adopting Williams's notation,

let ψ be the angle of incidence on the echelon of light of wave-length λ , positive in figure 4;

θ the angle of refraction in the plate;

α the angle of deviation of the diffracted beam, positive in figure 4;

μ the refractive index of plate relative to air for light of wave-length λ ;

t the thickness of the plate; and

s the width of the aperture and of the plate.

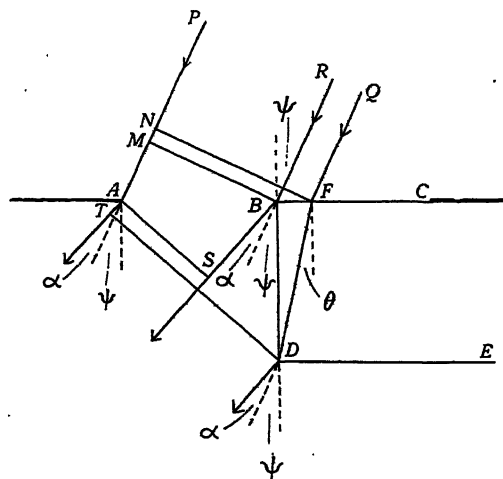


Figure 4. Diffraction of parallel beam by echelon: MB , AS and NF , TD , corresponding wave-fronts before and after transmission.

The intensity I_α of light of which the deviation is α is given by equations (2) and (4). In the present case X is half the phase-difference corresponding to $BS - MA$ and

$$X = \lambda^{-1}\pi s \{ \sin (\psi + \alpha) - \sin \psi \} \quad \dots\dots(5),$$

Y is half the phase-difference corresponding to $\mu FD - NA - AT$ and

$$Y = \lambda^{-1}\pi t \{ \mu \sec \theta - \tan \theta \sin \psi - \cos (\psi + \alpha) \} + X \quad \dots\dots(6).$$

We proceed to show that, as in the case of normal incidence ($\psi = 0$) $d\alpha/d\lambda$ is positive whether $d\psi/d\lambda$ be positive or negative.

For the m th order of interference of light of wave-length λ ,

$$m\lambda = t \{ \mu \sec \theta - \tan \theta \sin \psi - \cos (\psi + \alpha) \} + s \{ \sin (\psi + \alpha) - \sin \psi \} \quad \dots\dots(7),$$

or, since $\sin \psi = \mu \sin \theta$

$$m\lambda = t \{ \sqrt{(\mu^2 - \sin^2 \psi)} - \cos (\psi + \alpha) \} + s \{ \sin (\psi + \alpha) - \sin \psi \} \quad \dots\dots(8),$$

the root sign being essentially positive.

* F. B. Galitzin, *Bull. Acad. Sc. de St Pétersbourg*, 31, 67 (1905).

† W. E. Williams, *Proc. Opt. Convention*, Part 2, p. 987 (1926).

After differentiation with respect to λ and arrangement of terms,

$$\frac{m}{t} - \frac{\mu d\mu/d\lambda}{\sqrt{(\mu^2 - \sin^2\psi)}} = \frac{d\psi}{d\lambda} \left[\sin(\psi + \alpha) + \frac{s}{t} \cos(\psi + \alpha) - \cos\psi - \frac{\sin\psi \cos\psi}{\sqrt{(\mu^2 - \sin^2\psi)}} \right] + \frac{d\alpha}{d\lambda} \left[\sin(\psi + \alpha) + \frac{s}{t} \cos(\psi + \alpha) \right] \dots\dots(9).$$

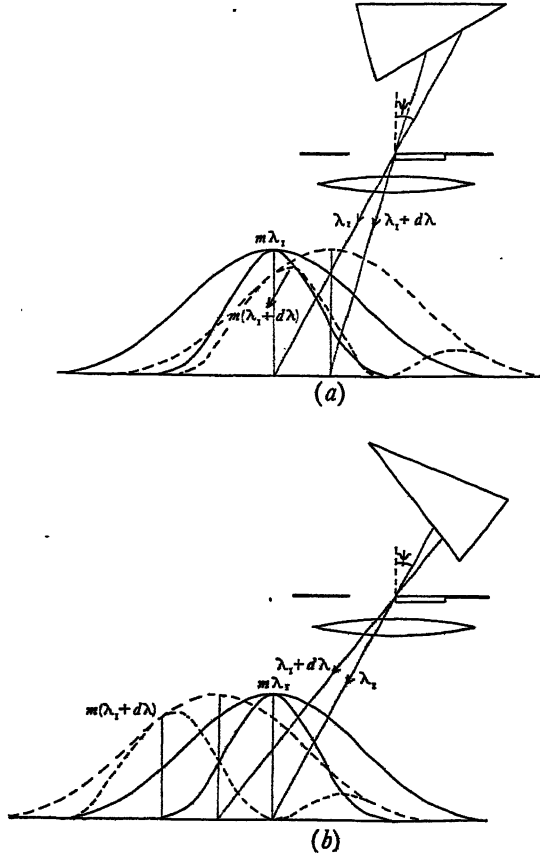


Figure 5. Echelon between prism and telescope. Intensity curves of m th orders of λ_1 and $\lambda_1 + d\lambda$. (a), $d\psi/d\lambda$ negative; (b), $d\psi/d\lambda$ positive. In both (a) and (b) $d\alpha/d\lambda$ is positive and numerically equal to $d\psi/d\lambda$.

Since $d\mu/d\lambda$ is negative, the left-hand side of equation (9) is positive. The coefficient of $d\alpha/d\lambda$ exceeds that of $d\psi/d\lambda$ by $(s/t) \cos\psi + \sin\psi \cos\psi/\sqrt{(\mu^2 - \sin^2\psi)}$, so that whether $d\psi/d\lambda$ be negative or positive $d\alpha/d\lambda$ is positive. In the case of normal incidence for all wave-lengths, previously treated, $\psi = 0$, and $d\psi/d\lambda = 0$, $d\alpha/d\lambda$ is positive; compare equation (3).

In figures 5a and b are shown the dispositions of prism and echelon for which $d\psi/d\lambda$ is negative and positive respectively, $d\psi/d\lambda$ is now identical with $d\phi/d\lambda$, the angular dispersion of the prism, and if it is numerically equal to the dispersion of the echelon while the m th maximum of λ_1 is supposed to be in the single-order

position, we have intensity-distribution curves comparable with those in figures 2*b* and 3*b*. The explanation of the asymmetry is seen to follow as before by reference to figures 2 and 3.

In terms of the present notation Porter* finds the condition that Y shall be unchanged when light of wave-length λ and incident at a small angle ψ is replaced by light of wave-length $\lambda + d\lambda$ incident at an angle $\psi + d\psi$, where the sign convention for ψ is opposite to that in the present notation—the condition, that is, that the m th order of λ shall coincide with the m th order of $(\lambda + d\lambda)$. This he finds to be $d\psi/d\lambda = (\mu - 1) t/\lambda s$. The explanation of the asymmetry is based on the fact that $d\psi/d\lambda$ must be positive. He points out that, even if the dispersions of echelon and prism are equal and opposite so far as the range of wave-length $d\lambda$ is concerned, perfect blackness of the dark bands will not in general be obtained. Light of wave-length λ is supposed to be incident normally on the echelon, and $m\lambda = (\mu - 1) t$. By using the above value of $d\psi/d\lambda$ it is concluded that in order that the $(m + 1)$ th orders of λ and $(\lambda + d\lambda)$ shall coincide m must be equal to 1, and a very thin strip would be required to make adjacent maxima correspond. In practice the author has found that with a glass plate 0.016 cm. thick and orders between 140 and 200 the dark bands may be very dark indeed provided that a suitable value of s is chosen. Doubt†, using a spectrograph of high resolving-power, has observed bands with a glass plate more than 9 cm. thick. Reference to figure 2 shows that provided that (i) the opposed dispersions of echelon and prism are equal for light whose wave-length lies between the wave-lengths λ_0 and λ_1 to which correspond consecutive bright bands, and (ii) the spread of the single-aperture curves for these wave-lengths is the same, the intervening dark bands should be perfectly black. According to Porter, for perfect blackness of dark bands within the range $d\lambda$ it is required that the interval between two successive maxima of I_α should be constant for the range. From figure 2 it is seen that, while the intervals between successive maxima within the ranges λ_0 to λ_1 , and λ_1 to λ_2 are not constant, perfect blackness is obtained since the intervals between successive minima are constant and it is supposed that these ranges are so small that the differences in spread of the corresponding single-aperture curves are negligibly small. Writing $m\lambda_1 = (m - 1)\lambda_0$ we see that $(\lambda_0 - \lambda_1)$ is inversely proportional to m , and so condition (ii) is the more nearly satisfied the smaller is $(\lambda_0 - \lambda_1)$ and, therefore, the greater is the value of m and the greater is the thickness of the plate. Even if the condition for perfect blackness were that the interval between two successive maxima should be constant, it can be shown that perfect blackness would be approached as the thickness increased, a conclusion directly opposite to that arrived at by Porter.

Suppose that light of wave-lengths λ and $(\lambda + d\lambda)$ is incident on the echelon at angles ψ and $(\psi + d\psi)$ respectively. Let the effect of the prism, so placed as to produce Talbot's bands, be to make the m th order maxima of λ and $(\lambda + d\lambda)$ coincide. We proceed to determine the conditions, so far as the plate-thickness t and the angle of incidence ψ are concerned, that the separation of the $(m + 1)$ th-order maxima of λ and $(\lambda + d\lambda)$ shall be as small as possible.

* *Loc. cit.*

† T. E. Doubt, *Phys. Rev.* 10, 322 (1917).

For small angles such that $\sin \beta = \beta$ and $\cos \beta = 1 - \frac{1}{2}\beta^2$ equation (8) assumes the form

$$m\lambda = t \left\{ \mu - 1 + \frac{1}{2}(\psi + \alpha)^2 - \psi^2/2\mu \right\} + s\alpha \quad \dots\dots(10).$$

If the m th order of λ is single as in figure 2 a

$$m\lambda = t \left\{ \mu - 1 + \frac{1}{2}\psi^2 (1 - 1/\mu) \right\} \quad \dots\dots(11).$$

If α_1 is the angular separation of the m th and $(m+1)$ th orders of λ

$$(m+1)\lambda = t \left\{ \mu - 1 + \frac{1}{2}(\psi + \alpha_1)^2 - \psi^2/2\mu \right\} + s\alpha_1 \quad \dots\dots(12).$$

From (11) and (12)

$$\alpha_1 = \frac{\lambda}{s + (\psi + \frac{1}{2}\alpha_1)t} \quad \dots\dots(13).$$

Hence when ψt is appreciable compared with s the separation of successive maxima is less than that (λ/s) between a central single-aperture maximum and an adjacent minimum, so that three orders appear in the so-called single-order position.

By differentiation of equation (13) with respect to λ we obtain an expression for the separation $d\alpha_1$ of the $(m+1)$ th orders of λ and $\lambda + d\lambda$

$$\frac{d\alpha_1}{d\lambda} = \frac{1 - \alpha_1 t d\psi/d\lambda}{s + \psi t + \alpha_1 t} \quad \dots\dots(14).$$

When the echelon is between collimator and prism, $d\psi/d\lambda = 0$ and $d\alpha_1$ decreases as t or ψ increases. Light of wave-lengths λ and $(\lambda + d\lambda)$ and of the same order will be deviated by different amounts. If the difference is $d\phi$ then, for coincidence of the m th and of the $(m+1)$ th orders of λ and $(\lambda + d\lambda)$, $d\alpha_1 = -d\phi$. The smaller $d\alpha_1$ the more nearly will this condition be fulfilled for light of intermediate wave-lengths. Hence perfect blackness is approached as t or ψ increases.

When the echelon is between prism and telescope, the angle of incidence on the echelon varies with the wave-length and $d\psi/d\lambda$ is identical with the angular dispersion of the prism. For coincidence of corresponding orders $d\alpha_1/d\lambda = -d\psi/d\lambda$. Then $d\alpha_1/d\lambda = 1/(s + \psi t)$ and again perfect blackness within the range $d\lambda$ is approached as t or ψ increases.

Considering the entire visible spectrum, the visibility of bands will vary since the dispersions of echelon and prism vary considerably in this wide range. The change in visibility is to be attributed to deviation from condition (i) above rather than to deviation from condition (ii).

The optimum value of s , the aperture-width for a given plate of thickness t , is found by equating echelon and prism dispersions. Denote the refractive indices of plate and prism materials by μ_e and μ_p . If T is the effective thickness of the prism for a beam of width $2s$ the prism dispersion $d\phi/d\lambda$ is $(T/2s) d\mu_p/d\lambda$. The echelon dispersion $\frac{d\alpha}{d\lambda} = \frac{m}{s} - \frac{t}{s} \frac{d\mu_e}{d\lambda}$ when the incidence is normal. Hence for wave-lengths in the neighbourhood of λ the best value of s is determined by

$$t \left(\mu_e - 1 - \lambda \frac{d\mu_e}{d\lambda} \right) + s\alpha = \frac{T}{2} \lambda \frac{d\mu_p}{d\lambda} \quad \dots\dots(15).$$

If consecutive bright bands occur at wave-lengths $\lambda_0, \lambda_1, \lambda_2$, etc. we may write *approximately*, as on p. 615,

$$(m-1)\lambda_0 = m\lambda_1 = (m+1)\lambda_2 = \text{etc.}$$

The angle of diffraction α of light of these wave-lengths will be zero, and by equation (8)

$$\begin{aligned}(m-1)\lambda_0 &= t \{ \sqrt{\mu_0^2 - \sin^2 \psi_0} - \cos \psi_0 \} \\ m\lambda_1 &= t \{ \sqrt{\mu_1^2 - \sin^2 \psi_1} - \cos \psi_1 \} \quad \dots (16),\end{aligned}$$

exactly, where $\mu_0, \mu_1, \psi_0, \psi_1$, correspond to λ_0, λ_1 . If the echelon is between collimator and prism, ψ is the same for all wave-lengths.

When the echelon is placed between the eye and the eyepiece of the spectroscope the plate must be placed on the side on which the violet appears, with the aperture towards the red. Consideration of the elementary theory of the eyepiece shows that in this case $d\psi/d\lambda$ is negative. If the echelon is reversed left and right $d\psi/d\lambda$ is positive and the asymmetry is readily accounted for as above.

The author has observed that when the echelon is placed in front of the spectroscope slit and illuminated by parallel white light so that the shadow of the edge of the plate falls on the slit, bands having the same appearance and spacing as Talbot's appear. Apart from a reduction in intensity of the bright bands there is no change in the appearance of the bands when the echelon is removed from a position immediately in front of the slit to a distance of one metre, the shadow of the plate-edge remaining on the slit. These bands are not subject to asymmetry of the Talbot type. If, however, the light transmitted by the echelon is focused on the slit, the bands may or may not exhibit asymmetry, according to the position of the image with respect to the edges of the slit. If the slit is so narrow that it does not admit the whole of the light corresponding to the single-aperture central diffraction maximum, the bands appear when the plate is either to the left or to the right of the slit. The same is true if the slit is wide and the chief diffraction maximum is partly intercepted by one side of the slit, but if the whole of this light is admitted the bands appear only when the plate is on the prism-base side of the slit.

To explain these effects it is necessary to refer to the fact that light of wave-lengths $\lambda_0, \lambda_1, \lambda_2, \dots$ corresponding to the centres of bright Talbot bands is in each case concentrated entirely in one single-order maximum. Such light is transmitted by echelon and collimator slit without deviation. Light of other wave-lengths is deviated right and left in the directions of the single-aperture subsidiary maxima, and is intercepted if the slit is not very wide.

In the case in which the Fraunhofer diffraction pattern is focused on the slit and the slit is wide enough to admit the main part of it the conditions are similar to those to which figures 2 and 3 refer, with the difference that the collimator lens produces a left-and-right inversion of the diffracted beams incident on the prism and the echelon must be placed with the plate on the prism-base side if the bands are to appear.

§ 3. OBLIQUE BANDS PRODUCED WHEN ECHELON AND PRISM DISPERSIONS ARE AT RIGHT ANGLES

If the echelon is placed between collimator and prism with the plate-edge horizontal and the slit is replaced by a small point aperture, the diffraction pattern observed consists of short bright and dark bands inclined to the horizontal at an angle which depends on the relative dispersions of echelon and prism. If the plate is below the aperture the bands are inclined upwards in the violet-to-red direction; if it is above, the inclination is downwards in the same direction. Corresponding to each bright band there are several fainter and shorter maxima similarly inclined. Oblique bands of this type have been photographed by Sethi* and by Beach*. The latter has accounted for the bands by means of vector diagrams. A very direct

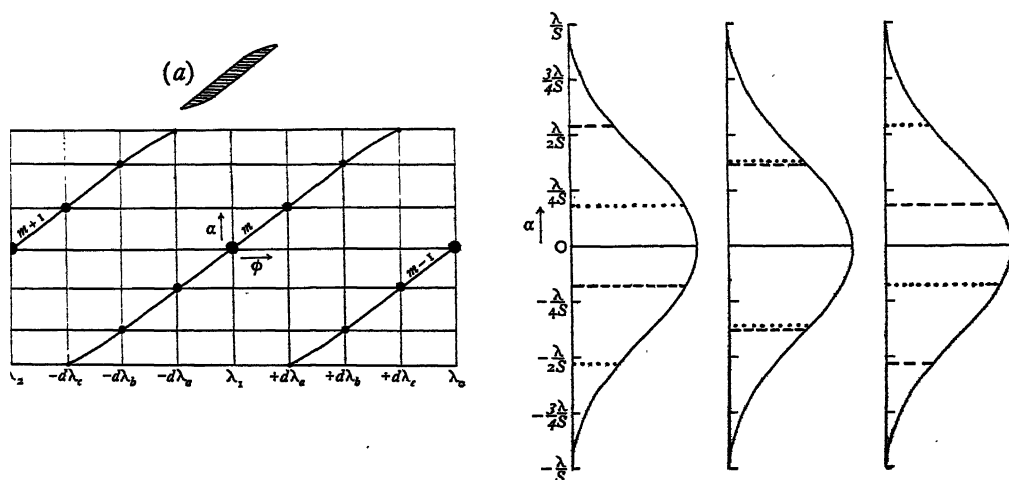


Figure 6. Echelon and prism dispersions at right-angles. (a) shape of main bright bands.

graphical representation of the mode of production of these bands is afforded by the method described in § 2 of this paper. In figure 6 the relative positions and intensities of maxima of I_α for various wave-lengths are shown, the echelon dispersion being vertical. On the left of the figure the resultant positions of the maxima after horizontal dispersion by the prism are represented by points whose sizes indicate the relative intensities. The actual shape of the main bands is shown at (a). The curvature near the ends is seen at once to be due to the fact that the rate of increase of vertical displacement of maxima of I_α diminishes appreciably near single-aperture minima.

§ 4. POWELL'S BANDS

The explanation of Powell's bands apparently is identical with that of Talbot's bands. Sethi*, however, using Stokes's* modified method of producing Powell's bands, obtained results which, he considered, showed that "the side of the cell on

* *Loc. cit.*

which the glass plate should be immersed relative to the prism is determined not by the relation between the refractive indices of liquid and plate but by the group velocities in the two media. Owing to the highly dispersive nature of the liquid employed in the experiments (a mixture of carbon disulphide and benzene), the position of the plate has on this account to be changed from one side to the other at a stage at which the refractive index of the liquid is still lower than that of the plate for the whole of the visible spectrum."

In further consideration of this reversal of Talbot asymmetry, let us examine the rate of change with wave-length of the order of interference between two corresponding normally incident rays of the same wave-length in air, λ_a , in the direction $\alpha = 0$, first when the media are glass and air, as for Talbot's bands, and then when the media are glass and liquid, as for Powell's bands. We shall assume the air to be non-dispersive and of unit refractive index.

Talbot's bands. $\frac{d}{d\lambda_a}$ (order of retardation of λ by glass—order of retardation of λ by air)

$$\begin{aligned} &= \frac{d}{d\lambda} \frac{t}{\lambda} (\mu_g - 1) \\ &= \frac{t}{\lambda_a^2} \left\{ \lambda_a \frac{d\mu_g}{d\lambda_a} - (\mu_g - 1) \right\} \end{aligned} \quad \dots\dots(17).$$

Thus, since $d\mu_g/d\lambda_a$ is negative, $dm/d\lambda_a$ is negative; that is, the greater the wave-length the smaller is the order-difference. Figures 2*a* and 3*a* are seen to be consistent with this result, for the order of $(\lambda_1 + d\lambda_a)$ that coincides with $m\lambda_1$ is less than m while the corresponding order of $(\lambda_1 - d\lambda_a)$ is greater than m .

Powell's bands. $\frac{d}{d\lambda_a}$ (order of retardation of λ_a by glass—order of retardation of λ_a by liquid)

$$\begin{aligned} &= \frac{d}{d\lambda_a} \left\{ \frac{t}{\lambda_a} (\mu_g - \mu_l) \right\} \\ &= \frac{t}{\lambda_a^2} \left\{ \lambda_a \left(\frac{d\mu_g}{d\lambda_a} - \frac{d\mu_l}{d\lambda_a} \right) - (\mu_g - \mu_l) \right\} \end{aligned} \quad \dots\dots(18).$$

This may be negative or positive. For a negative value

$$\mu_g - \mu_l > \lambda_a \left(\frac{d\mu_g}{d\lambda_a} - \frac{d\mu_l}{d\lambda_a} \right) \quad \dots\dots(19),$$

$d\mu_g/d\lambda_a$ and $d\mu_l/d\lambda_a$ are negative so that if the numerical value of $d\mu_l/d\lambda_a <$ the numerical value of $d\mu_g/d\lambda_a$ and $\mu_g > \mu_l$, then $dm/d\lambda_a$ is negative and the asymmetry is of the Talbot type.

But if $d\mu_l/d\lambda_a > d\mu_g/d\lambda_a$ numerically, $dm/d\lambda$ may be positive for a certain value of $\mu_g - \mu_l$ such that

$$\mu_g - \mu_l < \lambda_a \left(\frac{d\mu_g}{d\lambda_a} - \frac{d\mu_l}{d\lambda_a} \right) \quad \dots\dots(20).$$

In this case the progression of maxima as the wave-length increases is opposite to that indicated in figure 1 and the asymmetry is reversed.

The condition expressed by (20) for reversal of asymmetry is equivalent to that implied by Sethi*, which is that the group velocity of light in glass shall exceed the group velocity in liquid.

The group velocity, U , = $V_m - \lambda_m dV_m/d\lambda_m$, where V_m is the wave velocity of light of wave-length λ_m in medium m .

If V_0 is the velocity of light *in vacuo*,

$$\begin{aligned} V_m &= \frac{V_0}{\mu_m} \\ U &= \frac{V_0}{\mu_m} + \lambda_m \frac{V_0}{\mu_m^2} \frac{d\mu_m}{d\lambda_m} \\ &= V_0 \left(\frac{\mu_m + \lambda_m d\mu_m/d\lambda_m}{\mu_m^2} \right). \end{aligned}$$

Hence the condition that the group velocity in glass shall exceed that in liquid is

$$\frac{\mu_g + \lambda_g d\mu_g/d\lambda_g}{\mu_g^2} > \frac{\mu_l + \lambda_l d\mu_l/d\lambda_l}{\mu_l^2} \quad \dots\dots(21).$$

Since $\mu_m = \frac{\lambda_a}{\lambda_m}$ and $\frac{d\mu_m}{d\lambda_m} = \frac{\lambda_a}{\lambda_m (d\lambda_a/d\mu_m - \lambda_m)}$ this condition on further reduction becomes identical with equation (20).

* *Loc. cit.*

A DETERMINATION BY SPECTROMETER OF THE METRICAL THICKNESS AND DISPERSIVE POWER OF A THIN FILM

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ABSTRACT. By counting the numbers of Edser-Butler and Talbot bands produced within the same spectral range by a thin film of glass and a prism spectrometer, the metrical thickness of the film can be determined. The refractive index of the film for light of any standard wave-length can then be calculated from a count of the number of Talbot bands passing the position of the corresponding line in the spectrum as the Talbot echelon is rotated about the vertical edge of the film through an accurately measured angle. Two spectrometers are used in conjunction as a double-table spectrometer, and the other apparatus required is of the usual student-laboratory type. In the case of a film about 0.016 cm. thick the thickness is measured with an error not exceeding 0.0004 cm. and refractive indices are measured with an error not exceeding 0.0013.

§ 1. INTRODUCTION

IN the usual interferometer determinations of film-thickness the optical thickness, that is the product of refractive index μ and metrical thickness t , is measured. One method of determining t independently of μ in the case of a thin film whose thickness is of the order 0.01 cm. is to form an air wedge by placing the film between two accurately worked optical flats and to determine the angle of the wedge by measuring the separation of fringes formed by the interference of monochromatic light reflected at the wedge-surfaces. If it is required that the error of measurement be not more than 0.5 per cent, precision apparatus similar to that described by Smith* is necessary.

In the method to be described the thickness is determined by counting the numbers of Edser-Butler and Talbot fringes formed by the film between two well-separated spectral lines. The variation of refractive index with wave-length is measured by counting the number of fringes passing a spectral line as the Talbot film and aperture are rotated about a vertical axis through an angle which can be measured accurately. All the apparatus required is of student-laboratory type.

The method is based on the theory of the tilted transmission echelon†, for the film and aperture may be regarded as an echelon of two spaces‡.

* C. F. Smith, *Machinery*, October 27 (1927).

† F. B. Galitzin, *Bull. Acad. Sc. de St Pétersbourg*, 31, 67 (1905); W. E. Williams, *Proc. Opt. Convention*, 987 (1926).

‡ See p. 612.

§ 2. THEORY

Suppose the echelon to be placed between spectrometer collimator and prism in such a manner as to produce Talbot's bands, and let it be capable of rotation about a vertical axis through a measurable angle so that the angle of incidence of the beam of white light from the collimator upon the echelon may be varied and measured.

In figure 1 AB and $BCED$ represent the aperture and film respectively. Let PA and QF be corresponding rays of the incident beam; then if the relative retardation of these rays in the undeviated direction, after transmission, is an integral multiple of some wave-length λ_0 there will be a bright Talbot band corre-

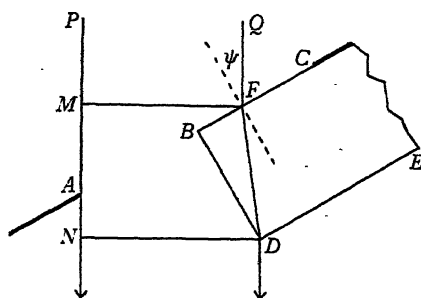


Figure 1.

sponding to this wave-length in the spectrum*. If FM is the incident wave-front and DN the parallel diffracted wave-front the retardation is

$$(\mu_0 FD - MN), \text{ which } = t\sqrt{(\mu_0^2 - \sin^2\psi)} - t \cos \psi$$

where t is the thickness of the film;

μ_0 the refractive index of film relative to air for light of wave-length λ_0 ; and ψ the angle of incidence.

Hence we may write $m\lambda_0 = t\sqrt{(\mu_0^2 - \sin^2\psi)} - t \cos \psi$.

If the next bright band occurs at λ_1

$$(m + 1)\lambda_1 = t\sqrt{(\mu_1^2 - \sin^2\psi)} - t \cos \psi$$

and for the n th bright band

$$(m + n)\lambda_n = t\sqrt{(\mu_n^2 - \sin^2\psi)} - t \cos \psi \quad \dots\dots(1),$$

μ_n being the refractive index corresponding to λ_n .

Between λ_0 and λ_n there will be n band-widths and

$$n = t \left\{ \frac{\sqrt{(\mu_n^2 - \sin^2\psi)} - \cos \psi}{\lambda_n} - \frac{\sqrt{(\mu_0^2 - \sin^2\psi)} - \cos \psi}{\lambda_0} \right\} \quad \dots\dots(2).$$

If

$$\psi = 0, \quad n = t \left\{ \frac{\mu_n - 1}{\lambda_n} - \frac{\mu_0 - 1}{\lambda_0} \right\} \quad \dots\dots(3).$$

* O. Darbyshire, the preceding paper (p. 611).

If Edser-Butler fringes are formed by placing the film in front of the spectrometer slit normal to the collimator axis and illuminating it by normally incident white light, the number p of fringe-widths between λ_0 and λ_n is given by

$$p = 2t (\mu_n/\lambda_n - \mu_0/\lambda_0) \quad \dots\dots(4).$$

Eliminating μ_n and μ_0 from equations (3) and (4) we have

$$t = \frac{p - 2n}{2 (\lambda_n^{-1} - \lambda_0^{-1})} \quad \dots\dots(5).$$

For normal incidence and a bright Talbot band at λ_s

$$m_s \lambda_s = t (\mu_s - 1) \quad \dots\dots(6).$$

Suppose the echelon to be rotated about the vertical edge of the film till the angle of incidence is ψ , and let the number of Talbot bands crossing the position λ_s in the spectrum be q ; then

$$\begin{aligned} (m_s + q) \lambda_s &= t \{ \sqrt{(\mu_s^2 - \sin^2 \psi)} - \cos \psi \} \\ &= t [\sqrt{(1 + m_s \lambda_s / t)^2 - \sin^2 \psi} - \cos \psi]. \end{aligned}$$

Squaring and simplifying the last equation we get

$$m_s = \frac{q^2 \lambda_s + 2qt \cos \psi}{2t (1 - \cos \psi) - 2q \lambda_s} \quad \dots\dots(7).$$

By means of equations (5), (6) and (7), t , μ_s and m_s can be evaluated.

§ 3. EXPERIMENTAL DETAILS

The film used was a piece of microscope cover-glass less than 0.02 cm. thick. Preliminary tests showed that over the area to be used the thickness was uniform and that Edser-Butler fringes of good visibility could be produced by transmission from a pointolite lamp of a parallel beam of white light incident normally on the film when the latter was placed immediately in front of the spectrometer slit. Talbot bands of a high degree of visibility were obtained when the widths of aperture and film-space were each about 1.3 mm. and the length 5 mm. The Edser-Butler fringes were so closely spaced that an accurate count by direct observation was tedious and difficult. The spacing of the Talbot bands was about six times that of the Edser-Butler fringes, but again a direct count of the number between standard spectral lines could not be effected as the standard lines were split into displaced component spectra by the echelon. Consequently both Edser-Butler and Talbot bands were photographed by means of a small constant-deviation spectrograph, and after exposure in each case the echelon was removed and a mercury-arc comparison spectrum photographed. To facilitate counting the numbers of bands between standard lines on the photographic plate a low-power travelling microscope was used. It was found possible to estimate to one-tenth of a band-width.

For the determination of orders of Talbot bands and refractive indices two good spectrometers of the usual student type were used. The usual adjustments were first made and then the two instruments were so placed as to act as a double-table

spectrometer, the unrequired telescope of one and the unrequired collimator of the other being turned aside, figure 2.

The echelon was mounted on a simple metal holder MH to be placed on the table T_1 of the spectrometer whose collimator was to be used. The film-edge E was adjusted for coincidence with the axis of rotation of the table by viewing it through a fixed low-power microscope and moving the holder until the edge appeared perfectly stationary when the table was rotated. On the table T_2 of the other spectrometer was a prism in the position of minimum deviation for the mercury green line. The telescope of this spectrometer was used for the observation of the bands. A pointolite lamp L was the source of white light, and the slit S could be illuminated by the mercury arc A by reflection from a glass plate P .

By use of the mercury lines and several other lines produced by salts in a Bunsen flame, a graph of telescope vernier readings against wave-length was first obtained. This was necessary because a bright band was not generally in exact coincidence

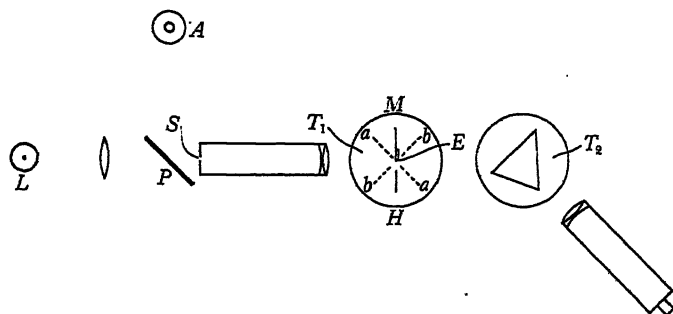


Figure 2.

with a standard line. From the difference of vernier readings for a standard line and the nearest bright band the corrected wave-length at which the bright-band-centre occurred could be estimated.

Rotation of the table and echelon clockwise from the position aa , figure 2, produced a motion of the bands across the spectrum from red to violet until the echelon was in the position of normal incidence when the motion stopped. Further rotation in the same direction towards the position bb caused the bands to cross the spectrum from violet to red. The position of the table corresponding to the stationary position of the bands was rather indefinite and in the measurement of the angle of incidence ψ the corresponding vernier reading was not used. To determine the order m_s of a bright band for normal incidence and occurring at some position λ_s in the spectrum by means of equation (7) it was necessary to measure the angle of incidence when from a count of the number q of bands passing the cross-wire the order of a band at the same position was known to be $(m_s + q)$. The cross-wire was set on the band in the stationary position. The table was turned from its position for normal incidence and stationary bands, first clockwise to bb , then counter-clockwise to aa , and the vernier was read in each case when the q th band passing in each case coincided with the cross-wire. Half the difference between the two readings was the angle ψ corresponding to q .

§ 4. RESULTS

Determination of t

p , number of Edser-Butler band-widths between λ_0 (5461 Å.) and λ_n (4358 Å.) = 231.0.

n , number of Talbot band-widths between λ_0 (5461 Å.) and λ_n (4358 Å.) = 42.5.

$$t = \frac{p - 2n}{(\lambda_n^{-1} - \lambda_0^{-1})} = 0.01576 \text{ cm.}$$

Table 1. Determination of m_s and μ_s

Standard line λ (Å.)	Corrected λ_s (Å.)	Number of bands q	Angle of incidence ψ (Deg. min. sec.)	Calculated order of band	Correct integral order m_s	Refractive index of film for light of wave- length λ_s μ_s
5791	5772	20	36 0 0	143.7	144	1.5274
		30	43 23 0	143.6		
		35	46 28 30	143.8		
		40	49 18 30	144.0		
5461	5453	20	34 58 45	153.3	153	1.5293
		30	42 10 30	153.4		
		35	45 14 15	153.2		
		40	48 1 0	153.2		
4916	4921	20	33 16 0	171.2	171	1.5339
		30	40 10 15	171.1		
		35	43 7 45	170.6		
		40	45 48 15	170.8		
4608	4603	20	32 11 45	183.6	184	1.5374
		30	38 53 0	184.1		
		35	41 45 30	183.7		
		40	44 21 45	183.8		
4358	4350	20	31 16 30	195.9	196	1.5410
		30	37 49 0	196.1		
		35	40 35 45	196.2		
		40	43 9 0	196.2		

n and p were measurable to one-tenth of a band-width so that t was accurately determined to 0.25 per cent. For a particular value of λ_s , the estimated values of m_s for four different values of q were never more than 0.4 greater or less than the same integer, so that the integral value of m_s was determined with certainty. The values of μ_s were thus correct within ± 0.0013 and fitted a smooth μ_s, λ_s curve and a straight μ_s, λ_s^{-2} line very well; from either of these graphs the dispersive power of the film in any region of the spectrum could be determined.

LOGARITHMIC UNITS: A NEED IN ACOUSTICS

BY A. H. DAVIS, D.Sc.

Received March 15, 1934.

ABSTRACT. In view of the confusion which prevails in the use of logarithmic units, the paper suggests the use of a new unit, to be named the "brig", for the ratio of two quantities, together with certain subsidiary changes, particularly in the nomenclature of acoustics.

THERE appears to be an urgent need for a convenient terminology for use when quantities are expressed in common logarithmic form. To meet the difficulty different branches of science tend to adopt special nomenclatures of their own, and although in some cases the requirements of the workers concerned may be met adequately, in almost all the meaning would be clearer to laymen if a common terminology were available. The name of Henry Briggs, the inventor of common logarithms, has a strong claim to adoption for the name of the unit*, and the following definition is therefore put forward: Two numbers N_1 and N_2 are said to differ by n brigs or $10n$ decibrigs when $n = \log_{10} (N_1/N_2)$.

On the above definition a 10-fold change in any quantity would be called a change of 1 brig; a change of 10^n -fold would be known as n brigs or $10n$ decibrigs, and so on. Wherever logarithmic expression is more appropriate or more vivid than other forms, the unit would be useful and informative†, although it would not necessarily displace all special nomenclature.

In the opinion of the writer, however, the position in acoustics has become such that the introduction of a purely mathematical logarithmic unit like the brig is urgently necessary. That a logarithmic terminology is needed in acoustics (the ear dealing comfortably with over a million-millionfold range of audible energy) has long been recognized. At least two units, the T.U. and the S.U., have been tried and abandoned as unsatisfactory. A unit called the "bel" is at present in vogue for representing a tenfold change of acoustical power but, possibly owing to acoustical associations of its name, it has come to be used also in a slightly different sense to represent the results of aural balancing of sounds, referred to later. Consequently many find difficulty in regarding it as a simple logarithmic unit even when it is used as such, and some suspect that it involves assumptions about the universal

* See A. H. Davis, *Discussion on Audition*, p. 82 (*Phys. Soc.* 1931).

† A change of 1 stellar magnitude is a change of 4 decibrigs in photometric intensity; a unit change of optical density in a photographic negative is a change of optical opacity of 1 brig; a vibrating system having a logarithmic decrement of δ would exhibit a decay in amplitude of vibration of 0.43δ brigs per cycle; radium decays in mass at a rate of about 1.8 centibrigs per century, or 5.5 micro-micro-brigs per sec.

validity of the Weber-Fechner law. In short, a position has arisen where precise statements are cumbersome, laxity is general, and confusion is common. The difficulty would be overcome if the brig were adopted for general use. If then a special unit, such as the bel, were required for any particular purpose in acoustics, it would be defined simply as a change of 1 brig in acoustical intensity. All readers would then understand that it was simply a term for convenient logarithmic expression of results, and the writer suggests that the term bel should be used as defined above, if at all.

It would be legitimate to apply the brig to express the extent to which one sound differed in intensity from a sound of unit intensity, thus " n decibrigs above unit intensity"; or from a sound of minimum audible intensity, thus " m decibrigs above threshold intensity."

A new term should, however, be adopted for use in aural measurements of the loudness of sounds, such as those where the loudness of a noise is measured aurally by observing the intensity-level of a note of standard pitch, say 1000 c./sec., which has been adjusted in strength until an observer has become equally aware of the noise and of the note.

In the past the bel, or more particularly the decibel, has been employed in expressing loudness-levels as well as intensity-levels. The practice has led to confusion and the writer tentatively suggests the adoption of, say, a "phon" defined* somewhat on the following lines: When an observer, listening simultaneously to a noise and to a note of chosen standard pitch having an intensity n decibrigs or decibels above the accepted threshold, judges that he is equally aware of the two sounds, the noise is said to have a loudness of n phons.

It will be realized that the two forms of expression for intensity and the term "loudness" are all useful. The first two express the intensity of a sound in brigs, but above different zeros. The third expresses the intensity of a comparison note which is as loud as the sound. Since the term *brig* or *bel* can be applied to the energy (intensity) of the noise, a different term *phon* has been chosen to express loudness, where in fact the energy of the noise is quite undetermined, and only the energy of a comparison note is expressed.

It is convenient to compare the above proposals with present practice, which appears to be to omit to mention the units and the zero when using decibels and to say:

an intensity-level of n decibels;

a sensation-level of n decibels;

a loudness of n decibels.

In general these levels are all different, and an increase of intensity-level by 10 decibels does not necessarily increase the loudness by 10 decibels: indeed the increase in loudness may even be 20 decibels. Consequently confusion arises as to the meaning and limitations of the decibel.

* As defined above, the phon is approximately the smallest loudness-change ordinarily detectable by the ear. The phon is in fact the German equivalent of the decibel. The present proposal is to use the word *decibrig* or *decibel* for intensity relations and *phon* for expressing loudness.

The writer, in his own published noise-measurements, has attempted to avoid the difficulty by more explicit forms of expression. He has for instance made it clear in his tables of noise-measurements that the decibels mentioned relate to the comparison note, not to the noise which was judged to be equally loud. The form of expression is almost impracticably cumbersome, however, and readers who have no time for elaborate niceties are apt to transfer the decibels to the noise without further ado.

If the proposals of the present paper were adopted the position would be distinctly clarified. One would say:

- an intensity of n decibrigs or decibels above unit intensity;
- an intensity of n decibrigs or decibels above threshold intensity;
- a loudness of n phons.

The nomenclature proposed would be consistent with the fact that an increase of 10 decibrigs or decibels in the intensity of a sound, as measured above unit intensity, would necessarily be accompanied by an increase of 10 decibrigs or decibels as measured above threshold. At the same time it would separate questions of intensity from questions of loudness, and would save a reader from the error of thinking that an increase of 10 decibrigs or decibels in intensity is necessarily associated with a 10-phon increase in loudness.

It is clear from the above that the essential requirements in acoustics are the quantitative relations which have been named the brig and the phon, one purely logarithmic and the other the basis of an aural scale. If the brig were adopted as a general mathematical unit, there would be no logical need for a special acoustical unit (bel) applicable to intensity and power. Its retention would depend upon the balance of convenience.

The writer suggests that the brig has a strong claim to adoption as a general mathematical unit for meeting the need, already acutely felt in acoustics, for a purely logarithmic form of expression.

A NOTE ON THE HYPERFINE STRUCTURE IN THE ARC SPECTRUM OF XENON

BY E. GWYNNE JONES, PH.D., Beit Research Fellow,
Imperial College of Science, London.

Communicated by Prof. A. Fowler, F.R.S., March 23, 1934. Read June 1, 1934.

ABSTRACT. The hyperfine structures of the Xe-I lines $\lambda\lambda$ 9045, 9799 and 9923 are described and analysed, and the hyperfine separations of the terms $2p_9$ and $2p_{10}$ are derived. It is also found that the lines $1s_5-2p$ are readily self-reversed. Previous nuclear spin data are confirmed.

§ 1. INTRODUCTION

THE hyperfine structures occurring in the arc spectrum of xenon, from λ 4400 to λ 8800, were described and analysed in an earlier paper by the present writer*. A new type of infra-red sensitive emulsion† has since made it possible to extend these observations into the region λ 9000 to λ 10,000, which contains the important Xe-I lines λ 9045 ($1s_5-2p_9$), λ 9799 ($1s_5-2p_{10}$) and λ 9923 ($1s_4-2p_9$). The analysis of the new line structures leads to the hyperfine structures of the terms $2p_9$ and $2p_{10}$.

§ 2. EXPERIMENTAL

As in the previous work, the xenon lines were excited in a Geissler tube (used in the side-on position with currents up to $5\frac{1}{2}$ mA.) and examined by means of Fabry-Pérot etalons mounted in a glass spectrograph. The photographs were all taken on Eastman I/Q (Xenocyanine) plates, exposure times of 3 to 9 hours being necessary.

§ 3. DISCUSSION OF RESULTS

The observed hyperfine structures of the lines $\lambda\lambda$ 9799 and $\lambda\lambda$ 9923 are shown in figures 1(a) and 2(a), in which the estimated intensities are represented by the heights of the appropriate lines, the positions being given in units of 10^{-3} cm^{-1} . The structure of λ 9799 is very similar to that of the next series member, λ 4792, but the resolution of the interferometer is so much greater in the infra-red that, in λ 9799, the components a and B are completely separated, figure 1(a) and plate (c). The structure of λ 9923 is like that of λ 4734 but on a much smaller scale, so that a and B now fall together, figure 2(a). In the case of λ 9045, which is considerably less intense than the other lines, only the three strongest components were observed

* E. G. Jones, *Proc. R.S.* 144, 587 (1934).

† C. K. Mees, *J. Opt. Soc. Am.* 23, 232 (1933).

(roughly -0.04 , 0 and $+0.04$ cm^{-1}). These components are sufficient to provide a check on the $2p_9$ term structure.

In agreement with the previous analysis, these line structures may be explained by assigning the nuclear moments $I = 0$ to the even isotopes, $I = \frac{1}{2}$ to Xe_{129} and

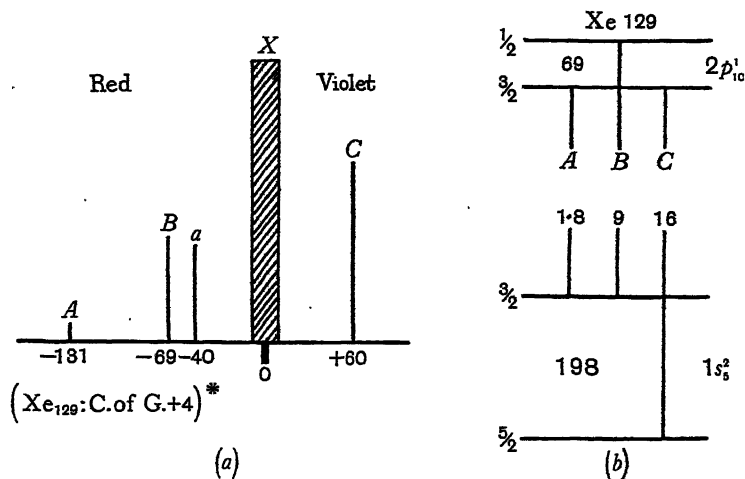


Figure 1. $\lambda 9799$ ($1s_5^2 - 2p_{10}^1$).

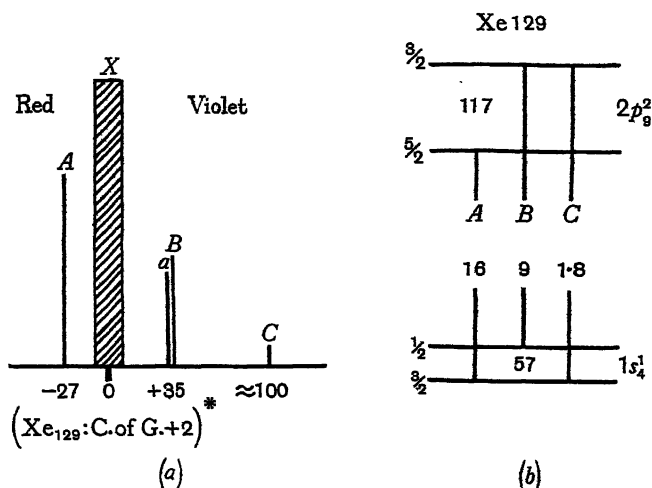


Figure 2. $\lambda 9923$ ($1s_4^1 - 2p_9^2$).

$I > 3/2$ to Xe_{131} . The complete analysis for Xe_{129} is given in figures 1(b) and 2(b). In figures 1(a) and 2(a) the components assigned to Xe_{129} are indicated by capitals and those to Xe_{131} by small letters. Since each of the lines represents a transition from an upper level ($2p_9$ or $2p_{10}$) of previously unknown structure to one ($1s_4$ or $1s_5$)

* The central component X is quite sharp and coincides with the centre of gravity of the components assigned to Xe_{129} .

of known structure, the hyperfine structures of the terms $2p_9$ and $2p_{10}$ may now be uniquely determined from the new data. The values thus obtained are shown in table 1.

Table 1

Term	J -value	Hyperfine separation of Xe_{129} (cm^{-1}) where $I = \frac{1}{2}$
$2p_9$	2	$-\bullet \cdot 117$
$2p_{10}$	1	$-\bullet \cdot 069$

§ 4. SELF-REVERSAL OF THE LINES

It has been found that all the lines $1s_5-2p$ ($\lambda\lambda$ 8231, 8409, 8819, 9045 and 9799) are very easily reversed. With currents as low as $\frac{1}{2}$ mA., all these lines are completely reversed when the tube is viewed end-on, but with the side-on arrangement no trace of self-absorption is found, even at $7\frac{1}{2}$ mA. It would thus appear that these lines should be used only with the greatest caution as comparison lines in grating spectra.

§ 5. DESCRIPTION OF PLATE

The hyperfine structure of the line λ 9799 is shown in the plate by means of three sets of etalon patterns. The resolution of the instrument increases with increased etalon separation, so that each pattern shows more detail than the preceding one. In plate (c) the dispersion is approximately $1/65 \text{ \AA./mm.}$

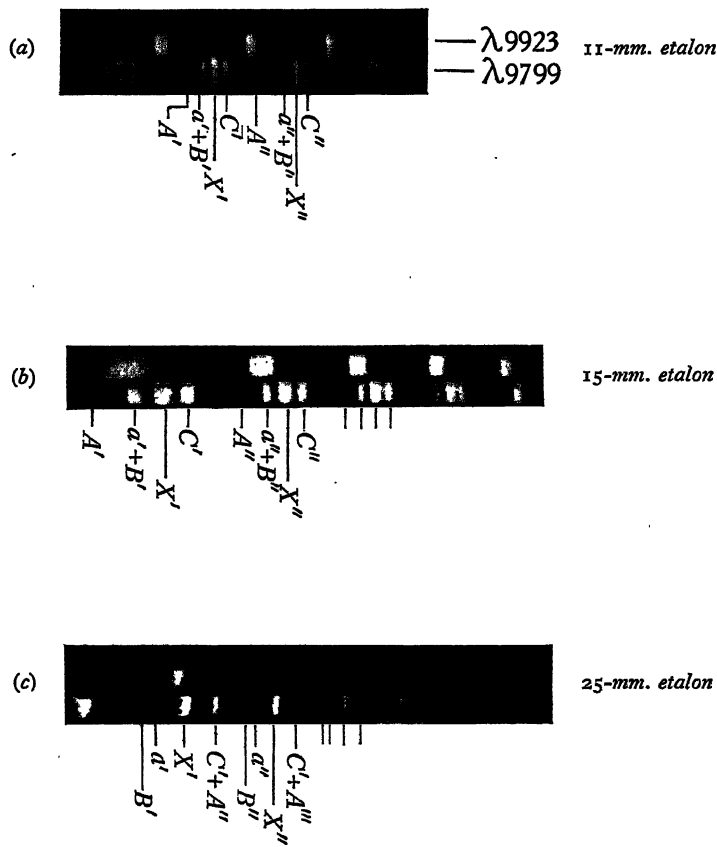
§ 6. ACKNOWLEDGMENT

The writer wishes to express his thanks to Prof. A. Fowler, F.R.S., in whose laboratories the work was done, for his kindly interest.

DISCUSSION

LORD RAYLEIGH said that the photographs were beautifully clean. Had the author had any trouble with the xenocyanine plates which he used? Some friends of the speaker had used them but had not obtained satisfactory results. It would be interesting to know how far into the infra-red a photographer could go. There was a tradition at the Imperial College that Sir William Abney had photographed a boiling kettle in the dark, but the photograph had never been on view. It was said that the Agfa Co. had produced plates allowing of a great extension of the solar spectrum in the infra-red.

AUTHOR'S reply. The reproductions do not show that the plates have a rather dense general fog which considerably increases the density of the negative, thus making it difficult to obtain a good print. This is not a great disadvantage in spectroscopic work but would restrict snapshotting activities to shorter wavelengths. It is, however, only fair to point out that the makers list the plates as "spectroscopic". The chief difficulty seems to lie in the rapid decrease in sensitivity during the first hour after the ammonia sensitizing. The Eastman plates go farther into the infra-red than any Agfa plates that I have used.



Etalon patterns of $\lambda 9799$ (see figure 1 a).

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A DETERMINATION OF THE ELECTRICAL CONSTANTS OF THE EARTH'S SURFACE AT WAVE-LENGTHS OF 1.5 AND 0.46 M.

By J. S. MCPETRIE, PH.D., A.M.I.E.E.,
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Communicated by Dr R. L. Smith-Rose, March 28, 1934. Read June 15, 1934.

ABSTRACT. A description is given of experiments made to determine the reflection coefficient and the electrical constants of samples of the earth's surface for radiation having wave-lengths of 1.5 and 0.46 m. It is shown that the most sensitive condition for finding the electrical constants of a substance from a study of its reflecting properties for electromagnetic waves is obtained when the radiation is incident normally on the reflector. The experiments described show that in this case the reflection coefficient of copper gauze is practically unity at both wave-lengths. There appears to be little difference in the reflecting properties of ordinary soil and soil covered by grass. It is suggested that the reason for this result may be that in both cases the bulk of the reflection takes place at a small distance below the surface. For radiation having a wave-length of 1.5 m. the dielectric constant of soil lies between 7 and 16 and the conductivity below about 10×10^8 e.s.u. This upper limit to the value of the conductivity is lower than that, 95×10^8 e.s.u., found previously on the same site at a wave-length of 1.6 m. Part of this discrepancy may be accounted for by the dryness of the season during which the present experiments were made. The results at a wave-length of 0.46 m. indicate possible values of between 7 and 20 for the dielectric constant and up to 40×10^8 e.s.u. for the conductivity of the soil.

§ 1. INTRODUCTION

MUCH interest has been taken in the last few years in the production of electromagnetic radiation at wave-lengths shorter than 3 m., corresponding to frequencies above about 10^8 c./sec. Very little attention, however, has been given to the propagation of the radiation produced. This propagation is intimately bound up with the electrical properties of any bodies such as the earth's surface or buildings present in the path of the waves. About the latter end of the nineteenth century many physicists made measurements on the electrical properties of different materials at these high frequencies, but the substances tested were not those which would affect the use of the waves for communication; moreover the experimenters had to be content with generators capable of producing only damped oscillations. With the modern three-electrode valve used as a Barkhausen-Kurz oscillator it is possible to obtain sustained oscillations of very high frequency. The present paper describes a series of experiments made at wave-lengths of 1.5 and 0.46 m. (frequencies of 2×10^8 and 6.5×10^8 c./sec.), in order to determine the

reflecting properties of typical samples of the earth's surface for radiation of these frequencies. In addition to being of some practical importance in determining the effect of the earth's surface on the propagation of waves belonging to this part of the spectrum, the type of experiment described can be made to yield valuable data on the characteristics of electromagnetic radiation close to a reflecting surface, represented in this case by the ground. The general study of propagation near reflecting surfaces will be pursued at a later date.

§ 2. PREVIOUS WORK

Smith-Rose and the author^(1,2) have made an experimental study of the electrical properties of the earth's surface for radiation at a series of wave-lengths between 10 and 1.6 m. In these experiments two waves from a local transmitter arrived at the receiver, one directly and the other after reflection at the ground. The field-strength at the receiver was measured for different distances between the transmitter and receiver while their respective heights above the ground remained constant. In this way a variation was obtained in the angle of incidence on the earth's surface of the ray reflected from the transmitter to the receiver by the ground. The observations were sufficient to determine approximately the coefficient of reflection at the earth's surface for this ray for a series of values of the angle of incidence. The electrical constants of the earth's surface for radiation having a frequency equal to that of the transmitter were then deduced from an application of Fresnel's equations for the reflection of electromagnetic waves by an imperfect conductor. The general result of this research was that over the range of wave-lengths observed the conductivity of the ground appeared to lie in the region of 10×10^8 e.s.u., corresponding to a resistivity of $900 \Omega\text{-cm.}$, for a typical field site for which experiments made at longer wave-lengths (about 300 m.) indicated a value of about 10^8 e.s.u. The dielectric constant could not be determined from the experiments and was assumed in the analysis to have a value of 10. Strutt⁽³⁾ has described similar experiments made on a wave-length of 1.42 m., from the analysis of which he was led to the same result—that the conductivity of the ground appeared to increase with increase in frequency of the incident waves.

§ 3. DESCRIPTION OF TRANSMITTERS AND RECEIVERS

Two separate transmitters were used for the two frequencies investigated. Both were of the type known as Barkhausen-Kurz oscillators, and as these are not very well known a short description of them is given. It is difficult to obtain oscillations from an ordinary valve circuit at wave-lengths shorter than about 2 m. It has been found, however, that oscillations of much shorter wave-length can be obtained if the valve used has cylindrical electrodes and if a high positive potential with respect to the filament is applied to the grid and a small positive or negative potential to the anode: in fact, a Barkhausen-Kurz valve oscillator, as such a transmitter is usually called, is somewhat similar to an ordinary retroactive valve-

oscillator in which the potentials applied to the grid and anode have been interchanged. There is one fundamental difference, however, which is that in a valve oscillator using retroaction the wave-length of the oscillations produced is controlled by the constants of the external circuit, whereas in the Barkhausen-Kurz type the wave-length is primarily dependent on the time of transit of the electrons between the electrodes of the valve and therefore on their dimensions and potentials. This feature was utilized in the experiments described below in the following way; two valves having different electrode-dimensions were chosen so that the same battery supply could be used to obtain radiation of two different frequencies.

The valve used in the higher-frequency oscillator was of the AT 40 type. Small variable condensers were placed between the grid and the two filament pins of the valve. These condensers were formed by fixing a small brass washer to the grid pin and similar washers on spindles to the filament pins. The latter could be rotated about the filament pins as axes so as to vary the terminal capacity between the grid and filament leads. The aerial was formed by a copper-rod extension of the anode pin in line with the anode support within the valve. With this arrangement strong oscillations were obtained at a wave-length of 0.46 m., when the grid-potential and current were maintained at 300 V. and 150 mA. respectively. A preliminary experiment showed that most of the radiation from the transmitter took place from the anode support and extension, which are considered in the analysis below to constitute the radiating source.

The longer-wave oscillator incorporated a valve of type ES 250. The anode in this valve was extended externally in the same way as in the oscillator described above, but in this case a small dry battery was fixed near the valve by means of which the anode was given a small negative potential with respect to the negative end of the filament. No tuning-condensers were used, because strong oscillations at a wave-length of 1.5 m. were obtained without them when the grid-voltage was 300 and the grid-current remained in the region of 220 mA.

The operating conditions of a Barkhausen-Kurz oscillator are so critical that unless they are maintained within narrow limits the oscillations cease. This feature was found to be very useful in the following experiments, for whether the transmitter was used continuously or intermittently the output remained constant to 1 or 2 per cent so long as the valve was giving rise to oscillations.

The receiver in each experiment consisted simply of a copper rod forming, with a 10-mA. non-contact thermojunction at its mid-point, a half-wave-length aerial. A d.-c. calibration of the thermojunction showed that the current output was very nearly proportional to the square of the heater current. In the analysis of the results this proportionality is assumed to be accurate at the high frequencies used.

§ 4. EXPERIMENTAL PROCEDURE

In the earlier experiments the transmitting and receiving aerials were arranged parallel to one another and a fixed distance apart in the same horizontal plane, figure 1. The output at the receiver was observed for different heights of this plane above the ground. Figure 2 gives a graphical illustration of the type of result obtained; it relates the reading of the microammeter connected to the thermo-junction at the receiver with the height of the plane containing the transmitter and receiver. It will be seen that as the height of this plane is altered the current at the receiver passes through a series of maximum and minimum values. The reason for this can readily be understood from a study of figure 1. In this figure T and R represent respectively the transmitter and receiver at a common height h above the ground. Radiation from T reaches R in two ways, one along the direct path

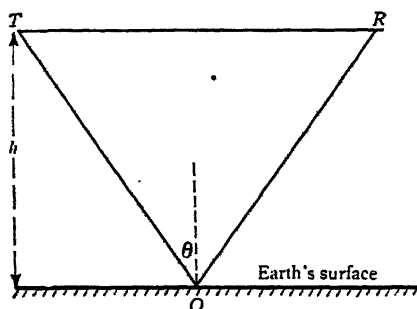


Figure 1.

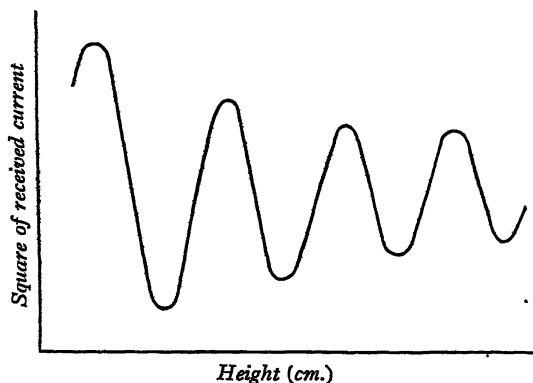


Figure 2. Graph illustrating relation between square of current in the receiving aerial and height above the ground.

TR and the other along the path TOR after reflection from the ground at O . The resultant magnitude of the field at R depends upon the amplitudes of these constituent waves and also on their phase-difference at R . This phase-difference depends on the actual path-difference between TR and TOR and also on the phase-change introduced on the ray TOR on reflection at the ground. The intensity of the resultant field at the receiver passes through maximum and minimum values respectively when the two waves at R are approximately in the same and in opposite phase. The difference in path between TR and TOR varies with change in the height h so that an interference pattern is obtained in the current received at R in the way shown in figure 2. The amplitude of the variation of the field-strength at the receiver decreases as the height h increases, for the effect of the reflected ray becomes small compared with the direct ray when the length of the path TOR becomes large compared with that of TR .

The phase-difference between the two waves at R is not merely that due to the difference in length of the two paths, for a phase-change is introduced in the ray TOR on reflection from the ground at O . This change of phase is dependent

on the electrical constants of the ground near O and also on the angle of incidence θ of the ray on the earth's surface. The amplitude of any wave reflected by the earth's surface is also determined by the constants of that surface and by the angle of incidence, the reflection coefficient increasing in general with increase in the value of the dielectric constant or conductivity of the reflecting substance. The exact positions of the peaks and dips as shown in figure 2 and, more particularly, their relative magnitudes are determined, therefore, by the reflection coefficient of the ground for radiation of the frequency used in the experiment. As the distance TR remains constant the angle of incidence θ changes with alteration of the height h . The electrical constants of the earth's surface are determined from such an interference pattern as figure 2 by finding those values from which the most closely similar curve can be obtained by theoretical analysis. This entails much tedious computation, for the reflection coefficient must be calculated for a sufficient number of values of the angle of incidence θ to determine accurately the positions and relative magnitudes of successive maxima and minima. The computation is much simplified if the angle θ remains constant as the height h is altered, since the reflection coefficient then has only one value. It can be shown theoretically that for a given change in the electrical constants of a reflecting surface the maximum change in the reflection coefficient occurs for normal incidence, that is when the angle θ , figure 1, is zero. The greatest sensitivity is obtained, therefore, in the determination of the electrical constants of the earth's surface when one aerial is arranged vertically above and parallel to the other. The amount of computation is then greatly reduced, since the formula for the reflection coefficient becomes relatively simple in the case of normal incidence and also its value remains the same for all heights of the transmitter and receiver.

The experiments were repeated, therefore, with the two aerials arranged horizontally and the transmitting aerial vertically above the receiver. Each aerial was fixed at the end of a horizontal beam and the two beams were attached to a vertical pole so as to remain at a constant distance apart. The lengths of the two beams and the distances between them were respectively 150 cm. and 250 cm. for the experiments on a wave-length of 1.5 m., and 50 cm. and 150 cm. when the wave-length was 0.46 m. The transmitting and receiving system could be moved as a unit up and down the vertical pole which had holes 5 cm. apart drilled in it. By means of a peg fitted beneath the lower beam to which the receiving aerial was connected, one observer could alter the height of the system and at the same time preserve a constant distance between the transmitter and receiver. The supply leads to the transmitting valve were twisted round one another and fixed to the wooden beam supporting the transmitter. They were supported on a post at some distance from the site of the experiment so that they remained sensibly horizontal and perpendicular to the transmitting aerial for all heights of the latter. No chokes were inserted in the supply leads, for the radiation from them to the receiver was found to be negligible. The microammeter at the receiver was placed at the vertical-pole end of the beam supporting the receiving aerial and was connected to the thermojunction by thin twisted copper leads.

The apparatus was set up so that the plane containing the transmitting and receiving aerials was vertically above the medium whose electrical properties were under investigation. The reading of the microammeter at the receiver was observed by telescope for different aerial-heights which were altered in steps of 5 cm. There is some doubt about the applicability of Fresnel's equations for points very near a reflecting surface and most of the observations were therefore made with the receiving aerials at heights of more than one wave-length above the ground. Interference patterns similar to that given in figure 2 were obtained. The reason for these is the same as that given above, except that in the present case the phase-change introduced on reflection at the ground remains constant since the angle of incidence is zero throughout the experiment.

§ 5. METHOD OF ANALYSIS

The conditions for maximum and minimum currents in the receiving aerial occur respectively when the two waves at the receiver are approximately in the same and in opposite phase. The coefficient of reflection at the earth's surface is complex; suppose its modulus to be of magnitude R . If the fixed distance between the transmitter and receiver is d and the observed height of the receiving aerial for maximum or minimum current is h then the measured current at this position should be proportional to

$$\left(\frac{1}{d} \pm \frac{R}{d + 2h} \right),$$

the positive or negative sign depending on whether the current observed is a maximum or a minimum.

The experimental results were plotted graphically in the form shown in figure 2 and the heights and amplitudes of the receiver-current maxima and minima were carefully determined. By adding the relations given by the above proportionality for the maximum-current conditions and repeating the procedure with the minimum, an average value of R was determined. Each series of experimental results was checked by determining the value of R obtained by means of different groups of maxima and minima. In this way any doubtful peaks and troughs could be eliminated when the average value of R was being found from the complete curve. The agreement between the different values of R was surprisingly good and usually sufficient to determine R with some certainty to the second significant figure.

The reflection coefficient, as has been mentioned before, is complex, and the above analysis determines its modulus only and not its two rectangular components. If the complex coefficient of reflection R be represented by $K + jK'$, the values of K and K' are deducible from Fresnel's equations for the reflection of electromagnetic waves at a conducting surface. In the case under consideration in which plane-polarized radiation is incident normally on the reflector the values of K and K' are given by the relations

$$K = \frac{1 - \sqrt{(\kappa^2 + 4\sigma^2/f^2)}}{1 + \sqrt{(\kappa^2 + 4\sigma^2/f^2)} + \sqrt{[2\{\kappa + \sqrt{(\kappa^2 + 4\sigma^2/f^2)}\}]}} \quad \dots\dots(1),$$

$$\text{and} \quad K' = \frac{\sqrt{[2\{-\kappa + \sqrt{(\kappa^2 + 4\sigma^2/f^2)}\}]}}{1 + \sqrt{(\kappa^2 + 4\sigma^2/f^2)} + \sqrt{[2\{\kappa + \sqrt{(\kappa^2 + 4\sigma^2/f^2)}\}]}} \quad \dots\dots(2),$$

in which κ and σ are respectively the dielectric constant and conductivity in electrostatic units of the reflecting surface for radiation of frequency f . When the conductivity (or the dielectric constant) of the reflector is infinitely great the component K' is zero and K becomes equal to -1 . This means that the wave undergoes a change in phase of 180° on reflection. When the reflector is an imperfect conductor the values of K and K' are negative and positive respectively. The advance of phase on reflection, equal to $\tan^{-1}(K'/K)$, is less than 180° and the amount of the change is a measure of the ratio K'/K . The magnitude of $\tan^{-1}(K'/K)$ was obtained in the present experiments by observing the displacement of the positions of maximum current from those deduced theoretically for the case of a perfect reflector.

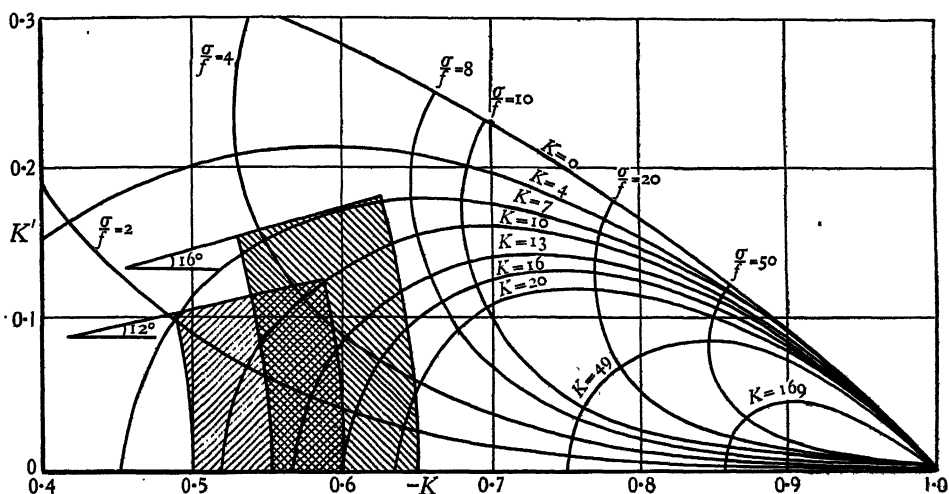


Figure 3. Curves giving the in-phase and in-quadrature components of the coefficient of reflection at zero angle of incidence for a medium having given electrical constants.

A determination of the magnitudes of the modulus of the reflection coefficient and the ratio of its two rectangular components is sufficient to determine the electrical constants of the reflecting surface under investigation. The two series of intersecting curves in figure 3 are obtained from relations (1) and (2) above by in turn assuming κ and σ/f as the constant and parameter, and *vice versa*, in these expressions. The point of intersection of any two of these curves determines the values of both K and K' for the common values of κ and σ/f for the two curves. In the same way corresponding values of κ and σ/f can be assigned to any point in the diagram. A knowledge of the modulus of the reflection coefficient and the value of $\tan^{-1}(K'/K)$ determines both the length of the radius vector from the origin of coordinates to a point and the angle this vector makes with the axis of abscissae. The position of the point is thus specified and, therefore, the values of both κ and σ/f for the reflector can be given. In any experiment there is always a certain limit to the accuracy of determination of both the reflection coefficient and

its components, so that the point required in the diagram degenerates into a small area which defines limits to the possible values of the electrical constants of the reflector. As has been mentioned above, the magnitude of K is negative. For convenience, however, the axes of coordinates in figure 3 have been arranged so that in this diagram an apparently small positive value for $\tan^{-1}(K'/K)$ represents actually an advance of phase on reflection of $180^\circ - \tan^{-1}(K'/K)$.

§ 6. DISCUSSION OF RESULTS

Determination of the modulus of the reflection coefficient for a wave-length of 1.5 m. Experiments were made on various typical substances. The analyses were performed in the way outlined above and the results are given in table 1.

Table 1

Date	Surface		Reflection coefficient
	Nature	Dimensions (m.)	
24. 7. 33	Grass	Field site	0.52
4. 7. 33	Soil	5 × 5	0.55
7. 7. 33	"	"	0.52
29. 8. 33	"	"	0.52
4. 7. 33	Iron wire netting of $\frac{1}{2}$ -in. mesh	1.8 × 4.0	0.98
4. 7. 33	Copper gauze	2.0 × 4.0	1.0

There appears from this table to be little difference between the reflecting properties of soil and those of ground covered by short grass. The reason for this may be that in each case the layer at which most of the reflection takes place is at a small distance below the earth's surface, but the experiments were not sufficiently accurate to determine whether this was actually the case. The small difference between the reflection coefficient of copper gauze and wire netting would indicate that although the use of a wire-netting screen under a transmitting aerial might be advisable at this high frequency, little extra gain in efficiency would be obtained with the much more costly copper screen. As the reflection coefficient of a given material usually increases with a decrease in frequency, wire netting should approximate even more closely to a perfect reflector for wave-lengths greater than 1.5 m. At long wave-lengths, however, the reflection coefficient of the earth becomes comparable with unity and little would then be gained by using either a copper or an iron wire-netting screen below the transmitting aerial.

Determination of the two components of the reflection coefficient for a wave-length of 1.5 m. The two components of the reflection are determined from the differences between the actual heights of the maximum- and minimum-current positions and the heights deduced analytically when the earth is assumed to be a perfect reflector. It was observed that although the amplitude of the reflected wave indicated that both copper gauze and iron wire netting were substantially perfect reflectors for the wave-length of 1.5 m., the positions of the peaks and dips of received current

did not correspond exactly with those found theoretically for a perfect reflector. Relations (1) and (2) above show that the values of K and K' are negative and positive respectively. This means that the retardation of phase on reflection must always be greater than 180° , and therefore that for an imperfect reflector the heights for maximum and minimum currents should be lower than those calculated for a perfect reflector in which the change of phase is 180° . There appears to be no satisfactory reason to account for the increase in heights observed in the case of the copper-gauze and wire-netting experiments. It may be due to the fact that the reradiation from the earth's surface is not quite plane at the receiving aerial. This would account for the direction of the displacement, but if it were the sole reason the discrepancy in height should decrease as the receiving aerial is placed at increasing distances from the ground. This result was not observed. Another possible but improbable explanation is that both screens had a capacitive reactance at the frequency in question.

When the results for soil and grass-covered soil were analysed the displacement of the peaks and troughs was found to be in the correct direction. There was little difference between the results for these two substances, the average displacement having a magnitude of about 3 cm. The unaccountable displacement in the case of the copper-gauze and wire-netting experiments was less than 2 cm. Assuming this latter displacement to be due to some propagation effect, then the maximum possible displacement for soil would be 5 cm. This latter value gives an upper limit to the phase-change on reflection and therefore to the value of the angle $\tan^{-1}(K'/K)$. A displacement of 5 cm. corresponds on a wave-length of 1.5 m. to a value of 168° for $\tan^{-1}(K'/K)$. All possible values of $\tan^{-1}(K'/K)$ for soil or grass, therefore, must lie between 180° and 168° . Suppose the accuracy of the experiment to be such that the reflection coefficient $\sqrt{(K^2 + K'^2)}$ for the soil and grass cannot be determined within closer limits than 0.5 to 0.6. All possible combinations of the values of K and K' must then lie within the sector of an annulus shown hatched in figure 3 and having an angle of 12° while the radii of the two circular sections are 0.5 and 0.6. It will be seen that with the limits given above the value of the dielectric constant of soil or grass must lie between 7 and 16 for radiation on a wave-length of 1.5 m. The upper limit to the value σ/f for the same substance is approximately 5. Figure 4 shows a comparison between the experimental results obtained for a grass-covered site and those obtained theoretically on the assumption that the values of κ and σ/f are 10 and 3 respectively, these values being approximately the mean of those possible according to the above analysis.

The dielectric constant of the ground is usually assumed to be 10 for long-wave radiation where its value is not critically important in determining the propagation of the waves. It is interesting to note that the mean value of the two limits given above is not far removed from this value. The value of 5 for σ/f corresponds for a wave-length of 1.5 m. to a value of 10×10^8 e.s.u. for the conductivity of soil*. Smith-Rose and the author^(x) gave a value of 95×10^8 e.s.u. as the conductivity of

* A conductivity of 10^8 e.s.u. corresponds to a resistivity of 9000 Ω -cm.

soil for a wave-length of 1.6 m. The present type of experiment is certainly more accurate than that from which this high value was determined: also the present experiment gives 10×10^8 e.s.u. as the upper limit to the value of the conductivity. The actual value, therefore, is probably less than that previously determined. Part of the discrepancy may be explained by the fact that the present experiments were made during an exceptionally dry season.

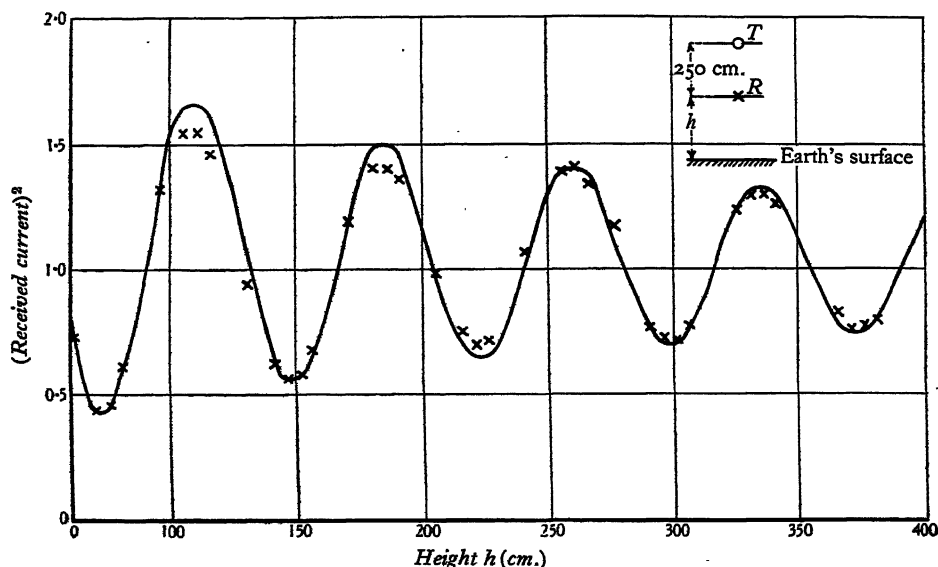


Figure 4. Relation between square of current in receiving aerial and its height above the ground.

x x Experimental values obtained July 27, 1933, grass, $\lambda = 1.5$ m.

— Theoretical curve calculated for $\kappa = 10$, $\sigma/f = 3$.

Determination of modulus of reflection coefficient for a wave-length of 0.46 m. Experiments carried out with a wave-length of 0.46 m. on the same sites as those detailed in table 1 yielded the results given in table 2.

Table 2

Date	Surface		Reflection coefficient
	Nature	Dimensions (m.)	
12. 5. 33	Soil	5 × 5	0.6
12. 5. 33	Copper gauze	2.0 × 4.0	0.94

The value of R for soil appears to be greater than that obtained for the wave-length of 1.5 m. This increase may be due to the fact that the experiments on 0.46 m. were made before the very dry period during which the experiments on 1.5 m. were carried out.

Determination of the two components of the reflection coefficient for a wave-length of 0.46 m. The determination of the two components of the reflection coefficient

of soil is more difficult for 0.46 m. than for the longer wave-length. This is due to the decrease in the accuracy of determination of the upper limit to $\tan^{-1}(K'/K)$. The average displacement of the positions of the peaks of current in the case of soil from those found for the copper gauze was approximately 2 cm., which gives a value of 164° for $\tan^{-1}(K'/K)$. If the reflection coefficient for soil is assumed from the experiments to lie between 0.55 and 0.65, the annular sector obtained in figure 3 is that given by the larger hatched area. It will be seen from this figure that the dielectric constant of soil for radiation of wave-length 0.46 m. then lies between 7 and 20. In the same way the upper limit for σ/f is seen to be 7. This corresponds to a value for the conductivity of approximately 40×10^8 e.s.u.

§ 7. CONCLUSIONS

The results of the series of experiments described above may now be summarized. The reflection coefficients of both a copper-mesh screen and half-inch-mesh iron netting appear to be approximately unity for radiation of wave-length of 1.5 m., and the reflection coefficient of copper gauze is still very high at 0.46 m. The experiments on a wave-length of 1.5 m. gave approximately the same value for the reflection coefficient of bare soil and that of soil covered by grass. It is to be assumed from this result that the bulk of the reflection in either case must take place in the soil itself. The dielectric constant of the soil for this wave-length appeared to lie between 7 and 16 and the conductivity below 10×10^8 e.s.u. The similar results on 0.46 m. indicate possible values between 7 and 20 for the dielectric constant and below 40×10^8 e.s.u. for the conductivity.

§ 8. ACKNOWLEDGMENTS

The work described in this paper has been carried out as part of the programme of the Radio Research Board and acknowledgment is due to the Department of Scientific and Industrial Research for granting permission for publication. The author is also indebted to Dr R. L. Smith-Rose for advice on the method of presentation of the paper, and to Messrs A. C. Haxton and H. M. Bristow for assistance in the experimental and computing work involved.

APPENDIX

Consideration of the difference between reflection at a perfect conductor and at a perfect dielectric

A study of figure 3 will show that when either the dielectric constant or the conductivity of a medium becomes great the value of K'/K approaches zero. In other words the phase-change $\tan^{-1}(K'/K)$ on reflection at normal incidence from such a medium is approximately 180° and, therefore, no observations made outside the medium under these conditions can determine absolutely whether the medium has a large conductivity or a large dielectric constant. The reason for this apparently

anomalous result is readily understood from a consideration of the boundary conditions. If the electric field at the surface due to the incident wave is E_1 in the first medium and E_2 in the second, denser, medium, then with the symbols given above

$$\{(1 + K)^2 + K'^2\}^{\frac{1}{2}} E_1 = (\kappa - 2j\sigma/n) E_2.$$

The right-hand side of this expression reduces to kE_2 when the second medium has a high dielectric constant, and to $-2j(\sigma/n) E_2$ when it has a large conductivity.

It will be seen that although the resultant field just outside the medium is the same in each case, the refracted waves differ in phase by 90° . No observations made with reflection methods at normal incidence and external to such a medium can determine, therefore, absolutely whether it has a high conductivity or a large dielectric constant. When reflection is obtained at angles of incidence other than zero the type of medium can be determined owing to the tangential boundary conditions. Maximum sensitivity would appear to be obtainable, however, if the wave within the medium could be observed. This suggests that when the reflection coefficient is high a laboratory method of investigation should be adopted so that the resistance and reactance of a given sample of the material may be found. From a knowledge of these two quantities the values of the dielectric constant and conductivity can readily be determined.

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THE MEASUREMENT OF THE ELECTRICAL CONSTANTS OF SOIL BY A LECHER-WIRE METHOD AT A WAVE-LENGTH OF 1.5 M.

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ABSTRACT. The paper describes an investigation carried out by means of a laboratory method of measuring the electrical properties of soil with alternating current of a frequency corresponding to a wave-length of 1.5 m. A parallel Lecher-wire system was set up and coupled to a source of oscillations of the desired frequency. The length of the stationary waves set up on the wires in air was measured and compared with the corresponding wave-length when the wires were immersed in the sample of soil under examination. The ratio of these wave-lengths gives directly a quantity involving both the conductivity and the dielectric constant of the soil. This quantity was measured for typical samples of Teddington soil having a wide range of moisture contents, and from the results deductions are made as to the values of the conductivity and dielectric constant of soil for various moisture-content conditions. Thus for conditions of normal moisture content the dielectric constant is found to have a value of 10 or 12, while the conductivity lies within the range 10 to 28×10^8 e.s.u. These values are in good agreement with those obtained by the use of a field method on the same site and at the same wave-length, and their accuracy is adequate for most purposes in connexion with radio communication.

§ 1. OBJECT OF THE PRESENT INVESTIGATION

IN two previous papers⁽¹⁾, the authors have described an investigation of the mode of propagation of ultra-short electric waves along the earth's surface. Over the wave-length range of 1.5 to 10 m. employed in this work, the electrical properties of the earth play an important part in determining the rate of decrease of field-strength with increase in distance from the transmitter. A comparison was made between the experimental results obtained and theoretical attenuation curves calculated on the basis of Fresnel's equations governing the conditions of reflection of electric waves from the boundary of a medium such as the earth; and in this way the investigation led to a determination of the electrical properties (conductivity and dielectric constant) of the earth for the wave-length range in question. The accuracy of determination of these quantities has been considerably improved by an extension of these field experiments in the manner described in the previous paper by J. S. McPetrie⁽²⁾. Measurements were made by him on the electrical

constants of the ground under conditions of normal incidence and for wave-lengths of 1.5 and 0.46 m.

The object of the experiments described in the present paper was to determine the electrical properties of samples of soil by a laboratory method on one of the wave-lengths previously employed in the field work referred to above. At wave-lengths above 30 m. the use of a laboratory method⁽³⁾ of measuring the conductivity and dielectric constant of samples of soil, or sea-water, has proved very successful as an alternative to the much more tedious and less direct field methods available for use on these longer wave-lengths. The method in question, however, which involved the measurement of the capacitance and resistance of a condenser filled with the sample under examination, is subject to considerable experimental difficulties when the wave-length is reduced to a few metres. An attempt was made, therefore, to study the properties of soil by observing the propagation of electric waves along a pair of wires embedded in a sample of the soil under investigation.

§ 2. THE PRINCIPLE OF THE METHOD EMPLOYED

The production of stationary electric waves on a parallel-wire system has been employed for the measurement of wave-length since the earliest days of radio-frequency research, for it was used in the classical work of Lodge and Hertz in 1888-1890 and later, and in more detail, by Lecher and Blondlot. This experimental method has also been applied by Heerwagen, Drude and others to the study of the dielectric constants of organic and inorganic liquids for wave-lengths of the order of 1 m.⁽⁴⁾ In the majority of these cases, damped oscillations were employed originating in a spark discharge, although it is highly desirable that the oscillations should be continuous and have, as far as possible, a pure sine wave-form. Among the more recent workers Southworth⁽⁵⁾ and Weichmann⁽⁶⁾ have successfully used the ordinary Lecher-wire method with continuous oscillations, corresponding to wave-lengths between 0.1 and 3 m., to measure the dielectric constant of water. In later work, Drake, Pierce and Dow⁽⁷⁾ have effected a refinement by using a concentric cylindrical system in place of the two parallel wires, and they have measured the dielectric constant of water with this arrangement for wave-lengths between 4 and 25 m.

In all this work the conductivity of the medium between the parallel wires was negligibly small, a condition which is no longer valid when the method is applied to the study of the properties of a material like soil. It is therefore useful to state briefly the theoretical basis of the method of employing stationary waves on parallel wires for the determination of the electrical properties of a medium which has an appreciable conductivity in addition to its dielectric constant.

It can be shown from the standard analysis of the propagation of alternating electric currents along a parallel wire transmission line that the voltage V_x at a distance x from the input end is given by an equation of the form

$$V_x = V_0 e^{-(\alpha + j\beta)x},$$

where V_0 is the input voltage to the line. In this equation α and β are known as

the attenuation and wave-length constants respectively. They are given by the equations:

$$\alpha^2 = \frac{1}{2} [\sqrt{\{(R^2 + \omega^2 L^2)(G^2 + \omega^2 C^2)\}} + (RG - \omega^2 LC)] \quad \dots\dots(1),$$

$$\beta^2 = \frac{1}{2} [\sqrt{\{(R^2 + \omega^2 L^2)(G^2 + \omega^2 C^2)\}} - (RG - \omega^2 LC)] \quad \dots\dots(2),$$

in which R , L , G and C are the primary constants of the line, i.e. the resistance, inductance, leakance and capacitance per unit length⁽⁸⁾, and ω is $2\pi \times$ the frequency f .

When the line is immersed in a pure dielectric such as air or water, $R = G = 0$ and we have:

$$\alpha = 0 \quad \dots\dots(3),$$

$$\beta = \omega \sqrt{LC} \quad \dots\dots(4).$$

Thus the length λ of the standing waves set up on the wire system is given by

$$\lambda = \frac{2\pi}{\beta} = \frac{1}{f \sqrt{LC}} \quad \dots\dots(5).$$

Assuming the medium to have unit magnetic permeability, the inductance of the wires will always be the value for immersion in air, whereas the capacitance will be proportional to the dielectric constant of the medium. If with oscillations of the same frequency f the lengths of the standing waves set up on the wires are λ_a in air and λ_s when the wires are immersed in the medium under investigation, then

$$\frac{\lambda_a}{\lambda_s} = \frac{\sqrt{L\kappa C}}{\sqrt{LC}},$$

whence
$$\left(\frac{\lambda_a}{\lambda_s}\right)^2 = \kappa \quad \dots\dots(6),$$

where κ is the dielectric constant of the medium.

Now suppose the wires to be placed in a medium of conductivity σ , the leakance G will no longer be zero and equations (1) and (2) reduce to:

$$\alpha^2 = \frac{1}{2} [\omega L \sqrt{(G^2 + \omega^2 C^2)} - \omega^2 LC] \quad \dots\dots(7),$$

$$\beta^2 = \frac{1}{2} [\omega L \sqrt{(G^2 + \omega^2 C^2)} + \omega^2 LC] \quad \dots\dots(8),$$

in which, using the suffixes s and a to apply to the constants of the wires in the medium and air respectively, we have

$$G_s = 4\pi C_a \sigma,$$

$$C_s = \kappa C_a.$$

Equations (7) and (8) now reduce to:

$$\alpha = \sqrt{\{\frac{1}{2}\omega^2 L_a C_a (\kappa' - \kappa)\}},$$

$$\beta = \sqrt{\{\frac{1}{2}\omega^2 L_a C_a (\kappa' + \kappa)\}},$$

where

$$\kappa' = \sqrt{(\kappa^2 + 4\sigma^2/f^2)};$$

and from equation (5)

$$\alpha = \frac{2\pi}{\lambda_a} \sqrt{\left(\frac{\kappa' - \kappa}{2}\right)} \quad \dots\dots(9),$$

$$\beta = \frac{2\pi}{\lambda_a} \sqrt{\left(\frac{\kappa' + \kappa}{2}\right)} \quad \dots\dots(10).$$

These two equations specify the attenuation and wave-length constants respectively of the standing waves set up on the wire under the conditions specified.

From equation (9) it is seen that the attenuation constant of the line increases continuously as the conductivity of the medium between the wires increases from zero towards infinity. Thus, for highly conducting media such as concentrated electrolytes, the amplitude of the waves set up on the wires decreases rapidly with distance from the source.

Equation (10) shows that the wave-length when the wires pass through the medium is given by

$$\lambda_s = \frac{2\pi}{\beta} = \lambda_a \sqrt{\left(\frac{2}{\kappa' + \kappa}\right)},$$

whence

$$\left(\frac{\lambda_a}{\lambda_s}\right)^2 = \frac{\kappa' + \kappa}{2} = y, \text{ say} \quad \dots\dots(11).$$

From this equation it is evident that a determination of the wave-length in air and in a medium such as soil gives the value of the quantity y or $\sqrt{\frac{1}{2}(\kappa' + \kappa)}$ which is a simple function of the electrical properties of the soil. If the attenuation constant of the waves could also be determined, the exact values of the conductivity σ and dielectric constant κ could be obtained with the aid of equation (9). The measurement of the attenuation constant is, however, more difficult than that of the wave-length although experiments in this direction have been made previously by M. Abraham⁽⁹⁾ and by M. J. O. Strutt⁽¹⁰⁾ at longer wave-lengths. Furthermore, exact determination of the actual values of σ and κ is not of very great practical importance, and the present investigation is limited therefore to the measurement of the wave-lengths in air and soil, and thus to a determination of the quantity $\frac{1}{2}(\kappa' + \kappa)$. A simple graph enables limiting values to be assigned to the quantities σ and κ to an accuracy which is sufficient for any practical case likely to arise in radio communication.

§ 3. EXPERIMENTAL PROCEDURE

The arrangement of the apparatus as finally adopted is shown in figure 1. Two hard-drawn copper wires of no. 14 s.w.g. were stretched horizontally at a distance apart of 2 cm. At one end the wires were terminated in a loop to enable the system to be coupled to the valve oscillator which was the source of the radio-frequency alternating current. At the other end the wires were connected through a non-inductive resistance equal to the surge impedance of the line, the effect of waves reflected at this end being thereby reduced. A wooden box of approximate dimensions 66 × 16 × 13 cm. was mounted as shown at (a), figure 1, with the two parallel wires threaded through thin keramot end-plates. This box could be slid along the wires so that the sample of soil under test could be placed in any desired position. The cross-sectional dimensions of the box are of some importance since, although the medium between the wires is the major factor determining the constants of the wires, these constants are also partly dependent upon the surrounding medium outside the wires. The effect of the surroundings decreases as either the

conductivity or the dielectric constant of the medium between the wires increases. The size of box used was adequate since it was found that the last few cm. of soil placed at the top of the box made no detectable alteration in the standing waves when the box was filled with dry soil, which is the most unfavourable case.

Three types of oscillator can be used in this experiment: (i) the ordinary retroaction type of valve oscillator such as was employed in the previous field work on a wave-length of 1.6 m.; (ii) an oscillator producing electronic oscillations on the Barkhausen-Kurz principle; and (iii) a magnetron oscillator. The oscillator of type (i) was found to produce only very weak oscillations at a wave-length of 1.5 m., this being its lower limit of operation. The electronic oscillator (ii), using a small cylindrical-electrode transmitting valve of the 40 to 250-watt type, was found to be a very convenient and simple source for demonstration purposes, and

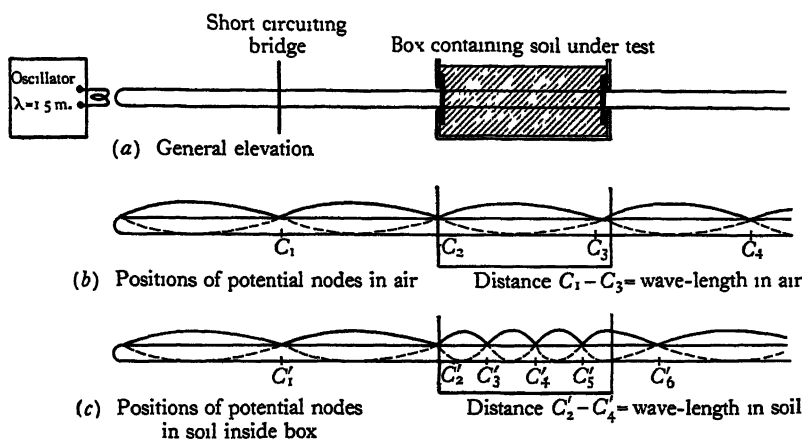


Figure 1. Diagrammatic illustration of standing waves on a Lecher-wire system in air and in soil.

was actually used at the Physical Society's Exhibition in January 1934⁽¹¹⁾, when the application of the Lecher-wire method to the determination of the dielectric constant of water was demonstrated. For more accurate working, however, it was desirable to have a greater amplitude of oscillation than is obtainable from this arrangement. A magnetron oscillator of the type described by E. C. S. Megaw⁽¹²⁾ was employed therefore for the majority of the final measurements on soil. The input end of the Lecher-wire system was coupled to the inductance of this oscillator, and the presence of standing waves on the wires was indicated by a small change in the anode current supplied to the valve. To obtain increased sensitivity the steady current flowing was balanced out in the well-known manner, so that the relatively small changes could be observed with ease.

When the medium under examination is a liquid, as was the case in all the previous work referred to in § 2, it is a simple matter to locate the position of the potential nodes by sliding the bridge along the wires in the liquid. When the medium is soil, however, such a method would entail considerable disturbance of

the soil, and so the following procedure was adopted. First, with the box empty, the positions of the potential-nodes (or current-antinodes) were determined by short-circuiting the wires with a copper bridge. When the bridge was in position at a potential-node, such as C_1, C_2, \dots , figure 1 (*b*), the Lecher-wire system was in resonance, and the increased load on the source was shown by the change in the deflection of the anode-current meter of the oscillator. The box was now moved so that its forward end coincided with the position of the node C_2 ; this ensured that there was no potential variation on the wires at this point, so that the effect of reflection at the boundary between soil and air would be reduced to a minimum. The distance between the successive nodes C_1, C_2, \dots provided a determination of the wave-length in air employed for the experiment. The box was now filled with soil and a continuous watch was kept on the positions of the nodes C_4, C_5, \dots on the wires on the side of the box remote from the oscillator. As the soil was placed around the wires the nodes C_4 and C_5 moved into the box into the positions C_4', C_5' as indicated at (*c*), figure 1. It was noted that this movement of the nodes was most affected by the soil placed in the immediate proximity of the wires, the soil at the bottom and near the top of the box having little effect. It was also observed that the nodes closed up appreciably as the soil was compressed, and the measurements were finally taken with the soil rammed as much as possible to simulate the conditions prevailing in the field.

When the box was filled with the sample of soil the positions of the nodes C_1' and C_2' were checked and the fresh position of C_6' was determined. If λ_a and λ_s are the wave-lengths in air and soil respectively, l is the length of the box and d the distance from the end of the box to C_6' at (*c*), figure 1, then we have:

$$\frac{l}{\lambda_s} = \frac{n\lambda_a - d}{\lambda_a},$$

where n is the number of whole wave-lengths between C_2' and C_6' .

$$\text{Thus} \quad \frac{\lambda_a}{\lambda_s} = \frac{n\lambda_a - d}{l} \quad \dots\dots(12),$$

and hence from equation (11)

$$y = \left(\frac{\lambda_a}{\lambda_s}\right)^2 = \frac{\kappa' + \kappa}{2} = \left(\frac{n\lambda_a - d}{l}\right)^2 \quad \dots\dots(13).$$

The above procedure thus enables a precise determination of the wave-length in soil to be made without the potential nodes in the soil being actually located, a process which would obviously entail some disturbance of the packed soil.

§ 4. DISCUSSION OF RESULTS OBTAINED

After the apparatus had been assembled and put into working order, a check was made on the accuracy of the method by using water as the dielectric. From the results obtained by previous workers, to whom reference has already been made, it is considered that the dielectric constant of distilled water is known to be 79. at 20° C. for wave-lengths between 1 and 10 m. This preliminary test with water

showed that the experimental determination of the position of the nodes could be made to an accuracy of a few per cent, which is quite adequate for the soil measurements undertaken. After the preliminary work, the wave-length employed was 1.5 m. for all measurements, and it was found that the corresponding wave-length in a specimen sample of surface soil taken straight from the ground was about 0.35 m. This wave-length is very dependent upon the actual moisture content of the soil, since it was already known from the work at longer wave-lengths that this factor influences to a considerable extent the conductivity and dielectric constant of the soil.

Accordingly, repeated measurements were made in the manner described on two samples of soil the moisture of which was gradually removed by a slow drying process. These samples were taken from just below the surface of an open field at the National Physical Laboratory, Teddington, and while in one case the soil was used in the condition in which it was removed from the ground with a moisture content of about 18 per cent, the second sample was artificially moistened with water to bring its moisture content up to nearly 25 per cent. Simultaneously with the electrical measurements, which were made daily on the two samples, a determination by weight was made of the moisture content, the results of which are expressed as the proportion of water to dry soil. All the measurements were carried out at a room-temperature of about 15° C.

The results of the measurements made on these two typical samples of soil are given in the graph forming figure 2, which shows the square of the ratio of the wave-length in air to the wave-length in soil, i.e. the quantity y in equation (11), plotted against moisture content. It is seen that y decreases from a value of about 23 for very wet soil to about 4 for very dry soil.

For moisture contents between 12 and 16 per cent, the broken line in figure 2 indicates a departure from the normal course of the full-line curve. Over this range it appears that the variation of the wave-length in soil with moisture content is much less than that indicated by the main curve, and the nature of the curve suggests the possibility of some resonance effect in the medium. The detailed examination of this suggestion has not yet been possible and this point must be left for later investigation.

Now the quantity y involves the conductivity and dielectric constant, both of which may vary with frequency and moisture content. Thus it is difficult to separate the individual values of σ and κ in the expression for y or $\frac{1}{2}(\kappa' + \kappa)$, but some very useful deductions may be made for the conditions which are of most practical importance. In the first place, previous work at longer wave-lengths has indicated that as the soil is dried out its conductivity decreases so rapidly as to render its effect negligible for moisture contents below 3 or 4 per cent. Thus the value of y for very dry soil is virtually the minimum value of κ for dry soil. In a similar way the previous work has indicated that the value of κ increases considerably with moisture content, and presumably it tends towards the value of 80 for pure water as the proportion of soil decreases to zero. The value of the dielectric constant for soil having a normal moisture content of about 20 per cent

is therefore greater than 4, the value obtained for dry soil in the present experiments, and it is probably several times this value. Now in figure 3 curves have been plotted showing the relation between σ/f and κ for various specified values of the quantity y . Thus if we take y equal to 20 for normal soil from figure 2, we see from figure 3 that $\sigma/f < 18$ since we know that $\kappa > 4$. For a probable value 10 of κ the corresponding value of σ/f is 14. In this way we can determine a definite upper limit and a probable lower limit of σ/f . Since the wave-length of 1.5 m. employed corresponds to a frequency of 2×10^8 c./sec., the limiting values of the conductivity of the ground are 36×10^8 and 28×10^8 e.s.u.

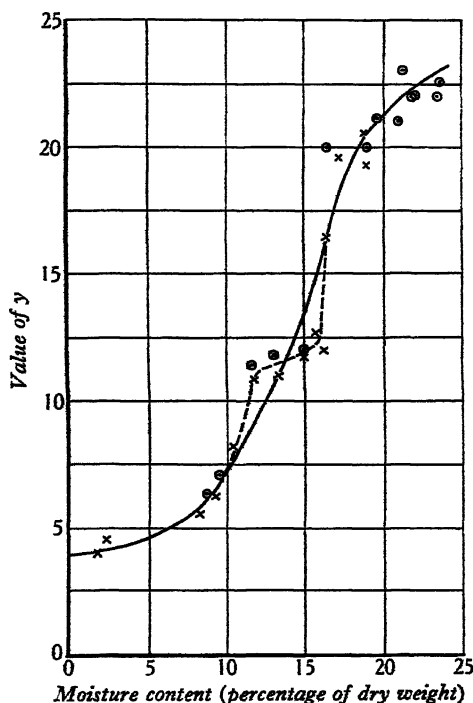


Figure 2. Relation between moisture content and value of y or $(\lambda_{\text{air}}/\lambda_{\text{soil}})^2$. \times Normal sample of surface soil. \circ Sample of soil artificially moistened.

In the preceding paper by J. S. McPetrie⁽²⁾, describing the field measurements carried out on the same wave-length of 1.5 m., it was deduced that the dielectric constant for soil or grass was between 7 and 16 while the conductivity was about 10×10^8 e.s.u. These experiments were carried out in the summer when the moisture content may be taken as about 16 per cent, which is the lower limit found for Teddington subsoil over a typical period of one year. For this moisture content the value of y obtained from figure 2 is about 14; thus the dielectric constant cannot exceed 14 in this case, while for the mean value (between 7 and 16) of 12 the corresponding conductivity is about 10×10^8 e.s.u. It is thus seen that the results obtained by the field and laboratory methods of measuring the electrical properties of the soil at a wave-length of 1.5 m. agree reasonably well when the variation in

these quantities with moisture content is taken into consideration. In one of the authors' earlier papers the use of a less accurate field method led to a value of the conductivity as high as 95×10^8 e.s.u. This is a possible value which might be accounted for by high moisture content, but the latest determinations are considered to be more accurate. In any case, however, all three determinations indicate quite definitely that at a wave-length of 1.5 m. the conductivity of the surface soil at Teddington is in excess of 10×10^8 e.s.u. as distinct from the values less than 2×10^8 e.s.u. obtained for wave-lengths above 30 m. The intervening gap between 1.5 and 30 m. has not yet been satisfactorily filled by a laboratory method, but research in this region is now in progress.

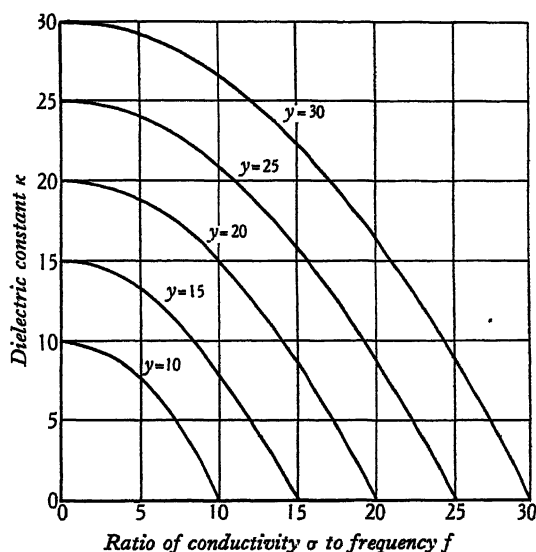


Figure 3. Relation between κ and σ/f for various values of y or $(\lambda_{\text{air}}/\lambda_{\text{soil}})^2$.

§ 5. ACKNOWLEDGMENTS

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THE THERMAL AND ELECTRICAL CONDUCTIVITIES OF METALS AND ALLOYS: PART I, IRON FROM 0° TO 800° C.

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ABSTRACT. A longitudinal-flow method has been used to determine the thermal conductivity, at mean temperatures ranging from 30° to 800° C., of a nickel-plated rod of Armco iron containing approximately 99.92 per cent of iron. After allowance for the effect of the nickel plating, and extrapolation to 0° C., a value of 0.177 c.g.s. units is obtained for the thermal conductivity of the iron. This value is higher than that usually attributed to iron, but a chemically prepared iron of greater purity has been examined also and found to have a thermal conductivity of 0.194 c.g.s. units at 0° C., and it seems evident that the lower results obtained by earlier investigators were due to the relative impurity of their specimens. The conductivity of Armco iron decreases with increase in temperature, the value at 800° C. being 0.071 c.g.s. units. By the use of values of the electrical conductivity which were determined during the same experiment as the thermal conductivity, the Lorenz function of this sample of iron has been calculated. It is found to increase from a value of 0.62×10^{-8} at 0° C. to the unusually high value of 0.74×10^{-8} at 400° C. and to remain approximately constant over the temperature-range of 400° to 700° C.

§ 1. INTRODUCTION

SOME eighty years have elapsed since Wiedemann and Franz* first propounded the law that the thermal conductivity of a metal is directly proportional to its electrical conductivity. In 1872 Lorenz† stated that the thermal conductivity was proportional to the product of electrical conductivity and the absolute temperature. This may be written

$$K/\sigma T = L,$$

where K is the thermal conductivity in c.g.s. units;

σ the electrical conductivity in $\text{ohm}^{-1}\text{-cm}^{-1}$;

T the temperature in degrees absolute.

L has been called the Lorenz constant, and several experiments‡ have been made to test the relationship. It is approximately true for a considerable number of metals at atmospheric temperature, although some of the poorer conductors appear to give an abnormally high value for L . At low temperatures, however, most metals fail to conform to the law. It is preferred on this account to refer

* *Ann. der Phys.* 89, 497 (1853).

† *Ann. der Phys.* 147, 429 (1872).

‡ *Handbuch der Experimentalphysik*, 9, pt 1, 207-11.

to L as the Lorenz function. Had the Wiedemann-Franz-Lorenz law been universally true, the relatively simple measurement of electrical conductivity or resistivity would have provided data for the calculation of the thermal conductivity and what is often a lengthy and difficult measurement could have been avoided. At present it is necessary to make accurate determinations of both the thermal and the electrical conductivity of as many conductors as possible over a wide range of temperature, in order to appreciate the range of validity of the above law and, perchance, to suggest modifications therein.

Two contributions to this subject have already been made from this laboratory. F. H. Schofield* made measurements on copper, magnesium, zinc, aluminium and nickel at temperatures ranging from about 100°C. to a maximum of 730°C. in the case of the nickel, and found that for the first three metals the Lorenz function was nearly constant at all temperatures while for the other two it increased with increase in temperature, a constant value being reached at about 300°C. in the case of nickel. E. Griffiths and F. H. Schofield† investigated a number of bronzes and light alloys from 80°C. to about 300°C. and found, with but one or two exceptions, that the value of the Lorenz function of the alloy was of the same order as that of the main constituent element. The method of experiment then employed to determine the thermal conductivity involved the measurement of the heat flowing through a rod of the material under test by means of a water-flow calorimeter attached to one end, and this definitely limited the range of temperature over which the determination could be made.

It was thought that the range of future experiments could be considerably increased by replacing the water-flow calorimeter by a metallic rod of known thermal conductivity. The following is an account of the determination over the range 0° to 800°C. of the thermal and electrical conductivity of a rod of Armco iron which is intended for use as such a thermal conductivity standard.

Choice of a thermal-conductivity standard. The chief requirements for a metal to be used as a thermal-conductivity standard over a wide range of temperatures are that it shall possess a high melting-point, remain unaffected by repeated exposure to high temperatures, and possess a thermal conductivity of the same order as that of the metals to be tested, which should either be independent of the temperature or vary approximately linearly with it. It is hoped to be able to carry out tests on some of the more poorly conducting metals which might be expected to have abnormally high values of the Lorenz function at room temperatures, and it appeared advisable for the standard material to possess a thermal conductivity between 0.03 and 0.3 c.g.s. units. The only pure metals which fall within this range and have a sufficiently high melting-point are iron, nickel and cobalt. Each of these metals possesses a magnetic transformation point at which a sudden change in conductivity might be anticipated. Cobalt has transformation points at about 460°C. and 1100°C. whilst that of nickel occurs at about 370°C. , so neither of these metals can be used. The effect of the transformation point of iron should not

* *Proc. R.S. A*, 107, 205-27 (1925).

† *J. Inst. Metals*, 39 (i), 337-74 (1928).

be unduly troublesome, for the point occurs at the upper end of the proposed temperature-range, and as iron of fairly high purity could readily be obtained in the form of Armco ingot iron, it was decided to investigate the thermal and electrical conductivity of this material.

§ 2. METHOD OF EXPERIMENT

The most suitable method for the determination of the absolute thermal conductivity of a metallic conductor at high temperatures appears to be one of the type employed by Schofield in the investigation to which reference has already been made. Heat is generated at a constant rate at the midpoint of a rod of the material under test. Leakage of heat to or from the surface of the rod is prevented by a surrounding guard tube, so that the whole of the heat supplied is operative in establishing a gradient of temperature towards each end. The measurement of these two gradients, the cross-sectional area of the rods, and the rate of supply of heat provide sufficient data for the calculation of the thermal conductivity. The author decided to use a method similar to this for the measurement of thermal conductivity and to arrange for measurements of the electrical conductivity to be made at the same time. Guided by the results of the above-mentioned work, the author considered it advisable to reduce the relative effect of any lateral gain or loss of heat, and thus to be in a position to measure the thermal conductivity of poorer conductors with greater accuracy, by using specimens about 3 in. in diameter, surrounded by a 6-in. guard tube. This increase in diameter naturally increased the heat capacity of the apparatus and thereby lengthened the time required for the attainment of steady conditions, but for the same gradient and conductivity it reduced the corrections per cm. for lateral heat-interchange to about one-tenth of those obtaining in the aforementioned experiments. A second advantage was that the temperature-gradient could be determined with greater certainty because, as will be explained later, it became practicable to measure all of the required temperatures by means of the same interchangeable thermocouple.

§ 3. PREPARATION OF SPECIMEN

Two similar rods of Armco ingot iron, each 3 in. in diameter and 42 in. long, were procured from the Armco International Corporation. An analysis of the turnings taken over a complete cross-section of the rod gave the following percentage chemical composition*.

Carbon	0.023
Silicon	0.007
Sulphur	0.020
Phosphorus	0.007
Manganese	0.025
Iron (by difference)	...		<u>99.918</u>

* The author is indebted to Mr T. E. Rooney of the Metallurgy Department for this analysis

One end of each rod was recessed to receive a heating-coil, as shown in figure 1(a), and was turned down to a mean diameter of 2.84 in. over a length of 15 in. At distances of approximately 6 and 25.4 cm. from this end holes 0.2 cm. in diameter were drilled to the centre of the rod to receive the thermocouple. The rods were then heavily nickel-plated over this machined portion by Messrs Fescol Ltd., and then again machined so as to have a final diameter of 2.895 in.

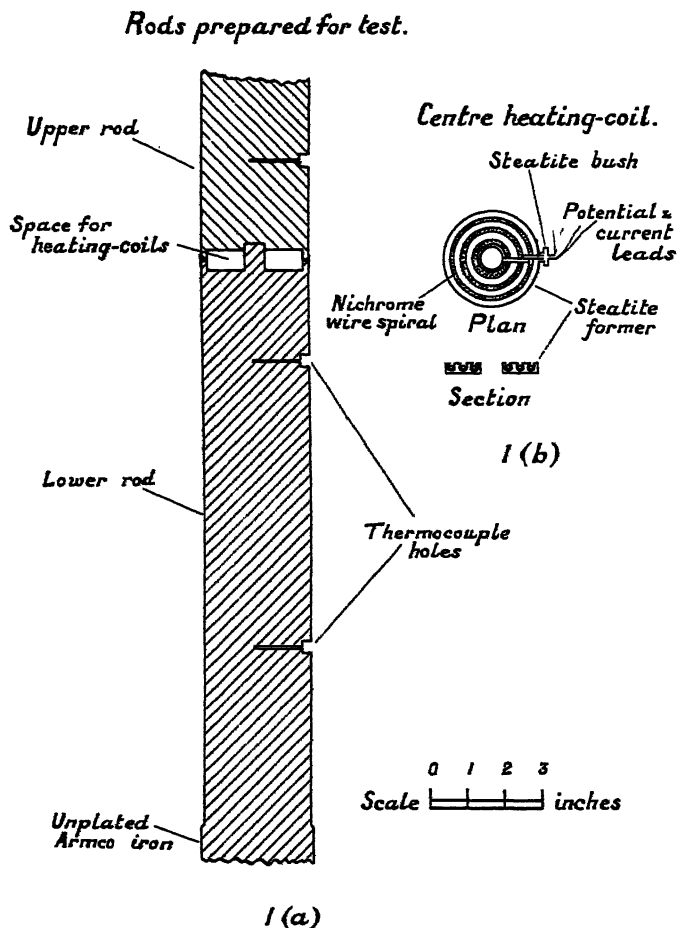


Figure 1.

Two similar heating-coils, each of approximately 22 ohms resistance, were prepared. One of these coils is shown in figure 1 (b). It consisted of a spiral of nichrome wire held in three concentric circular grooves cut in a disc of steatite which fitted closely into the cavity in the end of the rod. The steatite walls of these grooves converged at the top and projected above the nichrome wire, so as to prevent the possibility of short circuit between the wires and the specimen. The leads to each coil passed out through a specially designed insulator of baked steatite

inserted in a hole drilled in the side of the recessed portion in the rod. At a distance of approximately 1 cm. beyond this steatite insulator, current and potential leads were welded to the wires from the heating-coil, an atomic hydrogen arc being used for this purpose. The current leads consisted of 10 strands of nichrome wire of the same gauge twisted together, and the potential leads of a single strand of similar wire. When the two iron rods were mounted end-to-end the two heating coils became enclosed at the centre of the composite rod. Lateral displacement was prevented by means of a centre pin in the form of a $\frac{1}{2}$ -in. rod of iron. Holes $\frac{1}{2}$ in. in diameter were drilled through each rod at distances of about 2 in. from each unmachined end. These were to facilitate assembly and to provide sockets in which to insert the plugs of the current leads required for making the electrical conductivity measurements.

§ 4. DESCRIPTION OF FURNACE

The furnace consisted of a central iron tube $\frac{1}{4}$ in. thick, 6 ft. long and of 6 in. internal diameter, threaded for about a foot at the lower end to receive a heavy flange. The latter was bolted to a 2-ft. square base plate of iron $\frac{1}{2}$ in. thick which was supported at the corners by stout levelling-screws resting on four oak blocks 15 in. in height and bolted together by rods of $\frac{1}{2}$ -in. iron so as to form a rigid stand. A hole 7 in. in diameter had been cut in the centre of the base plate, and the tube was screwed down until about 9 in. projected below the base plate. This provided an exposed surface from which the rate of loss of heat could be readily controlled. A similar length was left exposed at the top of the tube, and the remaining central portion was covered with micanite and uniformly wound with nichrome tape. The windings of the furnace were tapped so as to be in seven sections which could be independently controlled, so that the temperature-distribution of the specimen could be accurately matched by that of the furnace tube. As a further aid towards this end an additional narrow heating-coil was wound on the centre section of the furnace tube. The turns of wire were so spaced as to enable four $\frac{3}{8}$ -in. holes to be drilled in a vertical plane of the furnace wall and in positions to coincide with the thermocouple holes drilled in the specimen. The whole of the windings were then covered with a layer of alundum cement.

Cylinders of sheet iron 11 in. and 23 in. in diameter, provided with holes for the passage of the heating-coil leads and the interchangeable specimen thermocouples, were then placed in position around the furnace tube. The nichrome leads were insulated by means of steatite bushes at the points where they passed through these cylinders and were finally bolted to a terminal board fixed in front of the furnace. A silica tube to serve as a sheath for the interchangeable thermocouple was inserted from the outside into each of the four holes in the furnace tube. The space between the furnace tube and the inner cylinder was then packed with sil-o-cel powder, and that between the inner and outer cylinders was packed with magnesia asbestos lagging.

Several thermocouples composed of 0.02-cm. platinum and 9:1 platinum-rhodium wires had previously been pegged into the inner wall of the furnace. These were insulated with twin bore silica tubing and the free ends of the wires were brought out at the top of the furnace.

§ 5. ASSEMBLY OF APPARATUS

The two halves of the specimen having been put together to form one continuous rod, with the two independent heaters enclosed in the central plane, six thermocouples composed of wire similar to the above were pegged into the test portion of the specimen and were insulated with twin-bore silica tubing supported alongside the rod so that the free ends were brought to the top. The method of pegging these couples consisted in welding the wires in an oxyhydrogen flame until the blob was just large enough to be firmly held in a small hole drilled in the surface of the rod by means of a no. 76 drill. The leads from the heating-coils were insulated with silica tubing and brought to the top. The specimen was then supported by means of a detachable framework and lowered into the furnace to rest on a small levelling table. The framework was removed, and the specimen was adjusted until it stood centrally within the furnace and the four tubes to protect the thermocouple could be inserted in their appropriate holes. The interspace between the specimen and furnace was finally packed with sil-o-cel powder to prevent the formation of convection currents. The apparatus so assembled is shown in figure 2. It will be observed that the ends of both specimen and furnace tube remain exposed to provide means for the control of the rate of loss of heat, additional cooling or heating units being fitted to these ends as required.

The circuit for the determination of the electrical conductivity was completed by connecting leads from the 110-volt d.-c. mains to the top and bottom of the specimen and including in the circuit a standardized resistance of $61.9 \times 10^{-6} \Omega$. and a controlling rheostat.

§ 6. DESCRIPTION OF THE EXPERIMENTS

To determine the thermal conductivity it was necessary to supply heat to the centre of the specimen and furnace in order to impose a gradient of temperature towards each end, and to adjust the various currents in such a way that when the steady state was attained corresponding points of specimen and furnace were at the same temperatures. This adjustment minimized any lateral transfer of heat and the whole of the heat generated at the centre of the specimen was then assumed to be operative in establishing the observed temperature-gradient. The temperature of the specimen was obtained by means of a thermocouple insulated by a 15-in. length of very fine twin-bore silica tubing which could be introduced through each of the four silica sheaths into the centre of the rod in these four positions. The electrical energy generated in the centre specimen-heaters was obtained by measuring the potential-drop across each coil and determining the current flowing

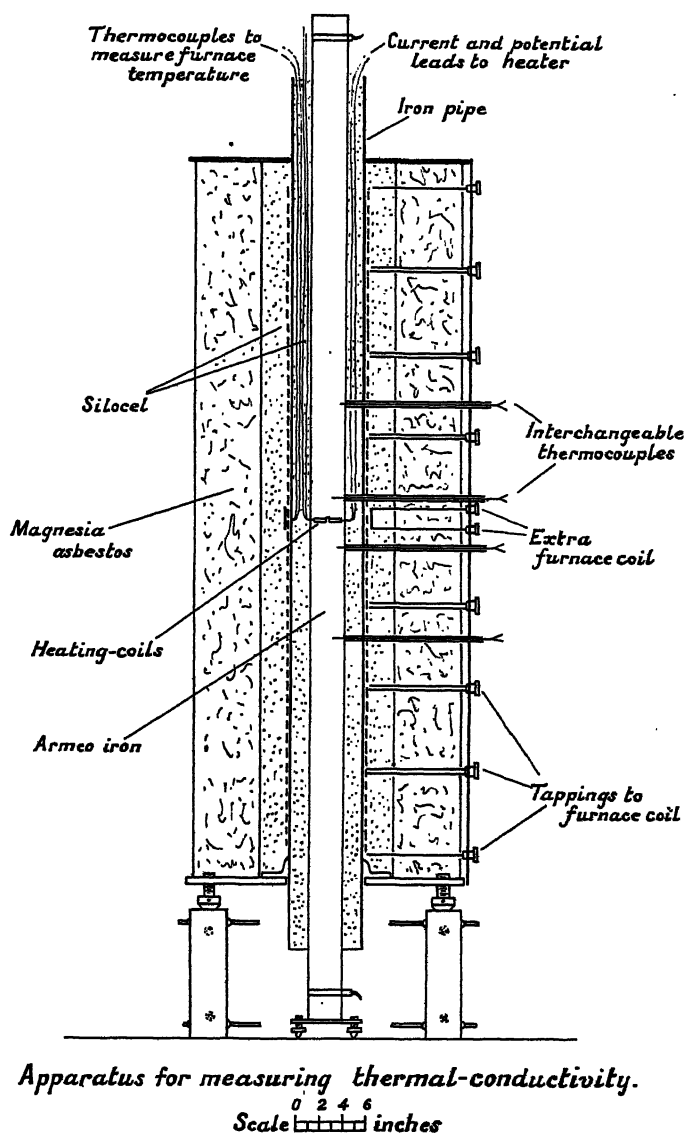


Figure 2.

in each in terms of the potential-drop across a standard shunt included in the same circuit. The thermal conductivity was calculated from the formula

$$K_{TS} = \frac{E_1 C_1 + E_2 C_2}{JA \{ (t_2 - t_1) + (t_3 - t_4) \} / l} \text{ c.g.s. units,}$$

where K_{Ts} is the thermal conductivity at the mean temperature T_s ;

E_1 and E_2 are the potential-drops across the two coils (V.);

C_1 and C_2 are the currents in the two coils (A.);

A is the area of the cross-section of the rod (cm^2);

t_1, t_2 and t_3, t_4 are the two temperature-measurements on the upper and lower halves ($^{\circ}\text{C.}$);

l is the distance between these pairs of couples (cm.); and

J is the Joule equivalent (assumed to be 4.184).

It was not always possible to obtain an exact agreement between the temperature of the furnace and specimen, so at each mean temperature apparent values were obtained for the thermal conductivity when the mean temperature of the furnace was a few degrees on either side of that of the specimen. These were then plotted to give the true thermal conductivity for an exact temperature-match.

Simultaneous measurements were made of the electrical resistance, a current of the order of 60 A. being employed for this purpose; and measurements of the potential drop on the specimen were obtained by inserting iron wires into the four thermocouple holes, readings being taken before and after reversal of the current so that the thermal e.m.f. due to the temperature-gradient in the rods could be eliminated. Detailed results are tabulated in the appendix, and all experimental values of the true thermal conductivity are shown plotted against the mean temperature in figure 3. The values of the electrical conductivity are similarly plotted in figure 4.

The first two runs were restricted to temperatures below 650°C. on account of failure of the centre heating-coils. In the third run this trouble occurred again after the specimen had been maintained at a temperature of about 800°C. for some days, and as steady matched conditions had not then been satisfactorily attained it was only possible to obtain electrical-conductivity data at the highest temperatures. The fourth run was without mishap and in addition to thermal and electrical conductivity-measurements up to 800°C. , check values during the final cooling were obtained. Between each run the apparatus was dismantled and reassembled. Some of the thermocouples which had been pegged into the furnace wall were broken during this process, and were replaced by new thermocouples either hanging freely close to the furnace wall, or moveable within lengths of thin-walled silica tubing. Reasonably good agreement was obtained between all three types of furnace couples. An examination of the experimental points plotted in figures 3 and 4 fails to reveal any serious change in either the thermal or the electrical conductivity occurring as a result of the heat treatment involved in the foregoing tests, from which it is concluded that the conductivity of the rods should remain unaltered in subsequent comparative tests within the range 0° to 800°C.

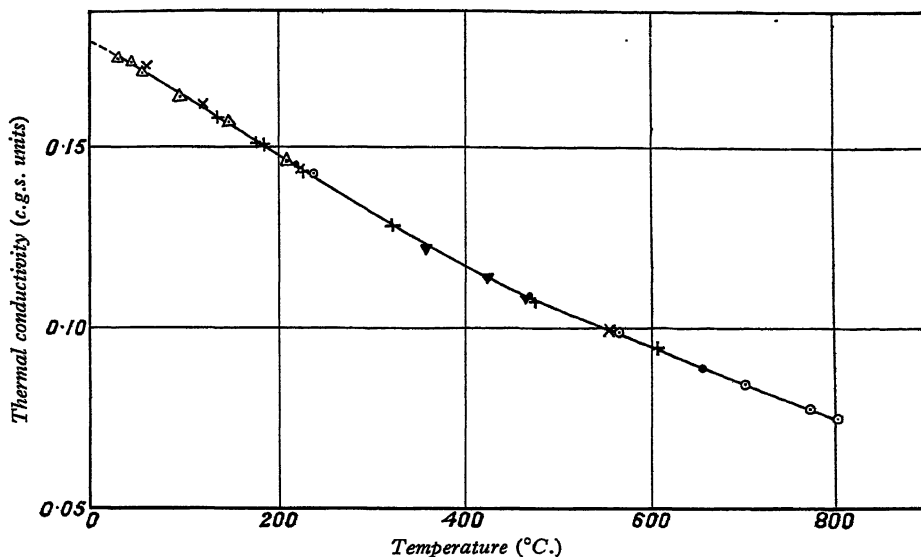


Figure 3. Variation of thermal conductivity of Armco iron (nickel-plated) with temperature.
First run: heating +; second run: cooling ▼; third run: heating ×;
fourth run: heating ○, cooling ●; alternative method Δ.

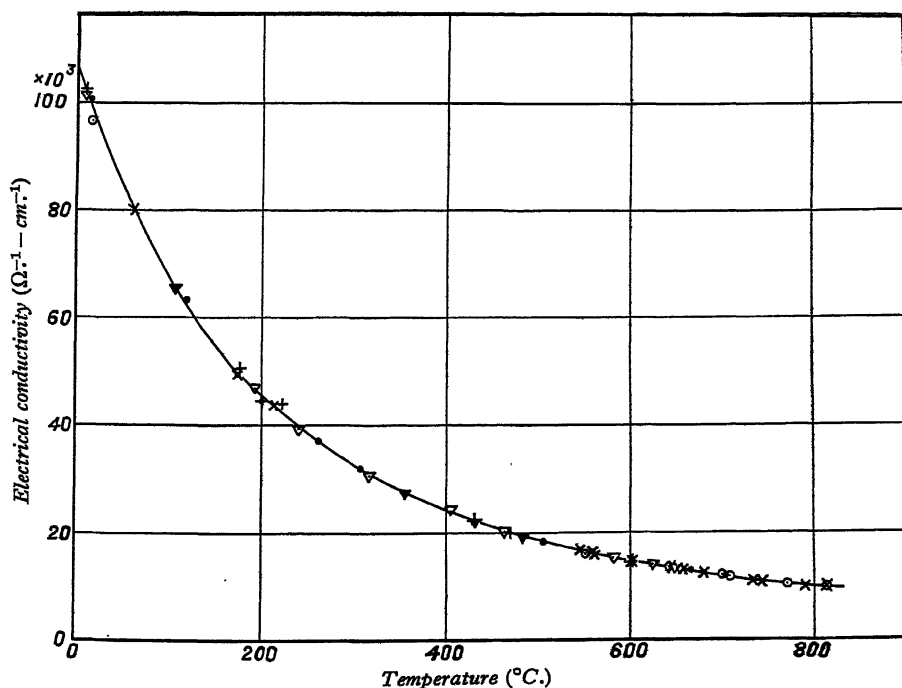


Figure 4. Variation of electrical conductivity of Armco iron (nickel-plated) with temperature.
First run: heating +, cooling +; second run: heating ▽, cooling ▼;
third run: heating ×, cooling ×; fourth run: heating ○, cooling ●.

§ 7. ALTERNATIVE METHOD USED OVER THE RANGE 30° TO 200° C.

A few additional determinations were made on one of the rods in which the energy was measured calorimetrically. The water was supplied at a constant rate and temperature to a cooling unit soldered to the plated end of the specimen. The increase in the temperature of the water during its passage through the cooling unit was measured by means of a differential thermocouple and it served, together with a knowledge of the rate of water flow, to determine the quantity of heat flowing from the rod. Precautions were taken to prevent lateral flow of heat by surrounding the rod with a guard tube. The values of the thermal conductivity obtained by this method also are plotted in figure 3. It will be seen that they are in good agreement with those obtained in terms of the electrical input, and that the method has enabled the experiments to be extended down to 30° C.

§ 8. ERRORS ARISING IN FOREGOING EXPERIMENTS

Every effort has been made to reduce to a minimum the lateral interchange of heat between the furnace and specimen. Apart from this there are the following possible sources of error to be considered: (i) loss of heat by conduction along the thermocouples and the current and potential leads; (ii) loss of heat by conduction in sil-o-cel insulation; (iii) loss of measured heat due to the fact that the potential leads were welded to the heating-coils at a point some 2 cm. outside the specimen; (iv) gain of heat due to the electrical energy generated in the leads to the heating-coils.

(i), (ii) and (iii) would tend to make the experimental value of the thermal conductivity too high, while (iv) would make it too low. The following paragraphs give an estimate of the probable error due to each cause.

(i) As all fixed thermocouples were brought out at the top of the apparatus, the loss of heat by conduction along those pegged into the upper half of the rod would be neutralized by the gain of heat by conduction along those pegged into the lower rod. All current and potential leads were also brought out at the top, and the gradient along them may be assumed to be the same as that of the top half of the specimen. Then, if the conductivity of nichrome is assumed to be comparable with that of iron, the conduction along the leads and the specimen will be proportional to their respective areas. The total number of strands of wire in the leads was 44, and as the diameter of the wire was 0.04 cm. the ratio of the areas is 0.0013. This indicates a probable error of 0.06, per cent since only half of the heat supplied has been considered. It is, of course, possible that the temperature-gradient in the current leads near the weld may be a little higher than that of the specimen at that point, but on the other hand the thermal conductivities of the leads and iron have been assumed to be equal, whereas at room temperature the conductivity of nichrome is about 16 per cent of that of iron, and at 800° C. it is some 75 per cent of the conductivity of iron. The heat conducted along the silica tubing insulating the current and potential leads is also quite small, since the area of the silica was only 0.3 cm^2 and its conductivity according to Seeman* varies from 0.0030 c.g.s.

* *Phys. Rev.* 31, 119-29 (1928).

units at 100° C. to 0.0057 at 800° C. It does not therefore seem probable that the error due to this cause can amount to more than 0.1 per cent.

(ii) The area of the sil-o-cel insulation is about three times that of the specimen. Its thermal conductivity probably varies from 0.00015 c.g.s. units at 100° C. to 0.00030 at 800° C. So, if one-third of the heat flowing in the insulation is assumed to have emanated from the specimen and the other two-thirds from the furnace, the error would amount to 0.1 per cent at room temperature and 0.4 per cent at 800° C.

(iii) The four potential leads were welded at distances away from the specimen ranging between 1.5 and 2.0 cm., so that the length of heating-coil outside the specimen would not exceed 8 cm. The total length of wire in the two heaters was 8 m., so that 1 per cent of the measured energy is actually generated just outside the specimen. As some of this heat would probably enter the specimen, the error on this account may be taken to be less than 1 per cent.

(iv) The current leads consisted of 10 strands, twisted together, of wire similar to that constituting the heating-coil and were found to have a resistance per unit length of approximately one-eighth that of the single wire. There were four such leads passing along the length of the top half of the specimen and carrying the same current as the heating-coil itself; that is, 100 cm. of current leads were alongside the working section of the upper half of the specimen. Therefore 1.6 per cent of the measured energy is generated in a wire alongside the specimen. A considerable proportion of this extra unmeasured heat might be expected to enter the specimen, but as this energy is distributed uniformly along the length, and the mean temperature-gradient has been measured, the error likely to be introduced would be less than $\frac{1}{8}$ of the above, i.e. less than 1 per cent. It would seem, therefore, that the total errors due to these four causes practically cancel one another.

There are also the following possible sources of error which do not involve heat leakage: (v) non-rectilinear flow of heat; (vi) incomplete accuracy of temperature-measurements; (vii) incomplete accuracy of electrical measurements; (viii) incomplete accuracy of linear measurements; (ix) change of dimensions with temperature; (x) effect of temperature-gradient.

(v) The heating-coils embedded in the centre of the specimen were designed to supply heat approximately uniformly over the cross-sectional area of the rods, and a distance of about 6 cm. was allowed before observation of the upper temperature, to enable rectilinear flow of heat to become established. Experimental confirmation that the flow of heat was rectilinear was given by an exploration of the temperature-distribution within each of the four thermocouple holes, uniformity of temperature being obtained in each instance.

(vi) The thermocouples were initially calibrated at the melting-points of mercury, sodium chloride and gold, and the boiling-points of water, naphthalene, benzophenone and sulphur. A small amount of contamination occurred in the

course of the experiments and this was probably due to unavoidable contact with the iron, but it was prevented as much as possible by efficient insulation with unbroken silica tubing. The calibration of the interchangeable thermocouple was frequently checked, and its junction was renewed from time to time. Measurements of the furnace-temperature were also made with this thermocouple, so that a true correspondence was obtained between the temperatures of the furnace and specimen.

(vii) The electrical measurements were correct to at least 1 part in 1000.

(viii) The holes into which the interchangeable thermocouple was inserted were 0.2 cm. in diameter and 19.4 cm. apart, and therefore error due to variation in the actual position of the thermojunction could not exceed 1 per cent. In practice multiple readings which would reduce this error were taken. No permanent change occurred in the dimensions of the working sections of the rods as a result of the heat treatment, but it may be mentioned that the unplated furnace tube became badly oxidized, and as a result its length increased by about 1 per cent.

(ix) If the value given in the *International Critical Tables* for the coefficient of linear expansion of iron is applied, the true thermal conductivity at the maximum temperature of 800° C. would be about 1 per cent lower than the value calculated from the dimensions at atmospheric temperature. As this effect is within the limits of experimental error, and will be partially neutralized in the contemplated comparison tests by the expansion of the material under investigation, no correction has been made on account of it.

(x) Both the thermal and the electrical conductivities have been measured in the presence of a temperature-gradient, and the values obtained have been assumed to be those for the mean temperature of the specimen. This is strictly true only when the conductivity is independent of temperature or varies with it in a linear manner. In the present instance the thermal conductivity decreases approximately linearly with increase in temperature, but the electrical conductivity does not do so. As, however, the temperature-gradient seldom exceeded 50° C., it is not anticipated that any appreciable error is introduced on this account. After consideration of all the likely sources of error, it would appear that the experimental values of both the thermal and electrical conductivities of the nickel-plated specimen of Armco iron are correct to within 2 per cent over the temperature-range 0° to 800° C. The values of the thermal and electrical conductivities obtained at intervals of 100° C. from the smooth curves drawn through the points in figures 3 and 4 are tabulated in columns 2 and 3 respectively of table 1.

§ 9. DISCUSSION OF THE RESULTS

A number of earlier determinations have been made of the thermal conductivity of iron, and it would be of interest to compare these with the results of the present investigation. Before this can be done it is necessary to apply a correction to allow for the presence of the nickel plating. In order to do this the values obtained for

the thermal and electrical conductivities of a sample of electrolytic nickel submitted for test by Messrs Castner Kellner Ltd. have been employed*.

The value of the thermal conductivity K , electrical conductivity σ , and specific resistance ρ , of the nickel-plated specimen and of the sample of Armco iron after allowance has been made for the effect of the nickel are tabulated for intervals of 100° C. in table 1.

Table 1

Temperature (° C.)	Nickel-plated Armco iron			Armco iron			
	K (c.g.s. units)	σ (ohm ⁻¹ -cm. ⁻¹)	ρ (ohm-cm.)	K (c.g.s. units)	σ (ohm ⁻¹ -cm. ⁻¹)	ρ (ohm-cm.)	L or $K/\sigma T$
0	0.179	106,500	9.4×10^{-8}	0.177	104,300	9.6×10^{-8}	0.62×10^{-8}
100	.164	67,400	14.8	.163	66,400	15.0	.66
200	.148	45,000	22.2	.147	44,300	22.6	.70
300	.132	32,300	31.0	.132	31,800	31.4	.72
400	.117	23,600	42.4	.116	23,200	43.1	.74
500	.105	18,500	54.0	.103 ₈	18,100	55.3	.74
600	.095	14,800	67.5	.093	14,300	69.8	.74
700	.085	12,000	83.3	.082	11,500	87.0	.73
800	.075	10,000	100.0	.071	9,480	105.5	.70

It will be observed that the correction which is necessary to allow for the effect of the nickel-plating becomes greater at the higher temperatures and amounts to about 5 per cent at 800° C. Below 400° C. the correction is small. The thermal conductivity of an unplated portion on one of the 3-in. rods was determined over the range 50° C. to 120° C. by means of the alternative method using the water-flow calorimeter. The results are included in the appendix, and it will be seen that the values obtained agree almost exactly with those for the nickel-plated portion. Several independent measurements of the electrical resistance of small rods of the Armco iron have since been made, and the value at 800° C. has been found to range from 104 to 106×10^{-8} ohm-cm. It is considered that the tabulated values for the thermal and electrical conductivity of Armco iron are correct to within 2 per cent.

The value of the thermal conductivity when extrapolated from 30° to 0° C. is 0.177 c.g.s. units, a value which is considerably higher than the commonly accepted value for pure iron. The weighted mean value of the thermal conductivity of iron according to the *International Critical Tables* is 0.148 c.g.s. units, whilst the range of probable values is considered to be 0.136 to 0.160 c.g.s. units. In this connection it may be remarked that insufficient attention appears to have been given to the state of purity of the iron. Among the earlier experimenters Lorenz† and Grüneisen‡ have found the thermal conductivity to be 0.165 and 0.172 respectively at 18° C.

* The author desires to acknowledge his indebtedness to Messrs The Imperial Chemical Industries (General Chemicals) Ltd., for permission to make use of these data, which it is hoped to publish in a later part of the work on this subject.

† *Wied. Ann.* 13, 438 (1881).

‡ *Ann. der Phys.* 3, 43 (1900).

and it is significant that the electrical resistances of their specimens at this temperature were 10.65 and 10.1×10^{-6} ohm-cm. These resistance values are lower than those of the majority of early investigators and suggest that the specimens employed were of relatively higher purity. In recent years this question of purity has been studied more closely. Benedicks, Bäckström and Sederholm* investigated a series of carbon steels; the purest, which contained 0.08 per cent of carbon, gave a resistivity of 10.55×10^{-6} at 18° C. and a thermal conductivity of 0.187 at 40° C. An analysis of the results indicated that pure iron should have a thermal conductivity of 0.227 at 40° C. and a specific resistance of 7.6×10^{-6} at 18° C. A similar investigation has been made by Masumoto† at a temperature of 34° C., the thermal conductivity of pure iron being given as 0.1741 and the specific resistance as 10.44×10^{-6} . Kannuluik‡ has recently investigated the thermal and electrical conductivity of Armco iron in the form of wire. The measurements were mostly carried out at low temperatures. At 0° C. his value for the electrical conductivity agrees closely with that of the present work, but his value for the thermal conductivity is about 5 per cent lower, being 0.1688 c.g.s. units. Sedström§ has obtained a value of 0.18 for a very pure electrolytic iron. Specimens of electrolytic iron have also been studied at low temperatures by Grüneisen and Goens|| and by Eucken and Dittrich¶. The former obtained values of the specific resistance at 0° C. ranging from 8.71 to 9.95×10^{-6} but he records no value of the thermal conductivity at this temperature. Eucken and Dittrich were primarily interested in the effect of grain-size on the conductivities. They gave values at 0° C. of 9.6×10^{-6} , 10.3×10^{-6} and 10.65×10^{-6} for the specific resistance and 0.225, 0.214, 0.196 for the corresponding thermal conductivities. These latter values appear to be remarkably high for the electrical conductivities with which they are associated.

It would seem from the foregoing survey of recent experimental work that the thermal conductivity of pure iron at normal temperatures is considerably higher than it was believed to be a matter of ten years ago. In this connection it is of interest to record that the present author has recently determined the thermal and electrical conductivities of a sample of very pure iron which had been chemically prepared in the Metallurgy Department of the National Physical Laboratory, and has obtained values of 0.185 c.g.s. units and 11.45×10^{-6} ohm-cm. at 50° C. which upon extrapolation indicate values of 0.194 c.g.s. units and 8.8×10^{-6} ohm-cm. at 0° C.

With regard to the data at high temperatures, so far as the author is aware the present thermal-conductivity determination is the first which has been made with a relatively pure sample of iron**. Honda and Simidu†† determined the thermal and electrical conductivities of a number of carbon steels up to about 900° C. but the

* *J. Iron and Steel Inst.* 114 (ii), 127-75 (1926).

† *Proc. R. S.* 141, 159 (1933).

‡ *Z. f. Physik*, 44, 615-42 (1927).

† *Sci. Rep. Tōhoku Univ.* 16, 417 (1927).

§ *Inaug. Diss. (Lund) Stockholm* (1924).

¶ *Z. Phys. Chem.* 125, 211-28 (1927).

** Since this paper was written results for the thermal-conductivity of several irons over the temperature range 100 to 500° C. have been published by S. M. Shelton, *B. S. J. of Res.* 12, 441 (1934). The thermal conductivity of the purest sample studied, which contained 99.90 per cent of iron, is in close agreement with that of the present investigation.

†† *Sci. Rep. Tōhoku Univ.* 6, 219 (1917).

specific resistance of their purest iron (Swedish iron) at 0° C. was as large as 15.3×10^{-6} , and the thermal conductivity of this sample decreased from 0.134 at 30° C. to 0.077 c.g.s. units at 800° C. It will be observed that the conductivities agree fairly closely at high temperatures, a fact which will be more fully dealt with in a later publication.

§ 10. THE LORENZ FUNCTION

The values obtained of the Lorenz function for Armco iron have been recorded in the last column of table 1 and are plotted in figure 5, in which the values of a number of other investigators also are included. The curve for copper, based on the results of Meissner* and Schofield†, are included for comparison. It will be

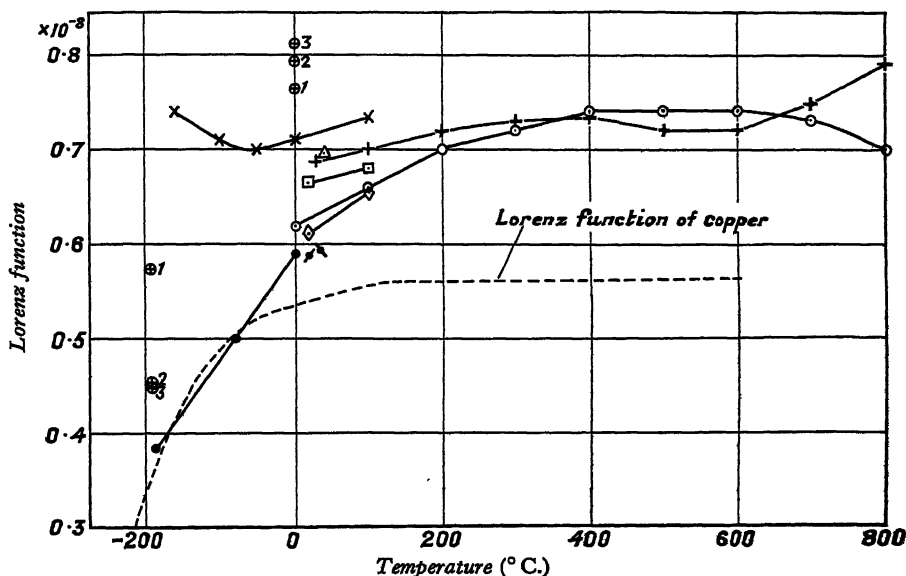


Figure 5. Variation of Lorenz function of iron with temperature.

⊕ Eucken and Dittrich. ✕ Grüneisen. + Honda and Simidu. □ Jaeger and Diesselhorst.
• Kannuluik. × Lees. ◇ Lorenz. ↘ Masumoto. △ Sederholm. ⊙ Present author.

observed that a considerable range of values has been obtained and that whereas the Lorenz function of the impure iron examined by Lees† increases as extremely low temperatures are approached the Armco iron tested by Kannuluik behaves similarly to copper at low temperatures in that the Lorenz function decreases rapidly with decrease in temperatures.

In the case of copper the value of the function becomes practically constant over the range from atmospheric temperature to 600° C. but the present experiments show the value for iron to be somewhat greater at normal temperatures and

* *Deutsch. Phys. Ges. Verh.* 16, 262 (1914).

† *Loc. cit.*

‡ *Phil. Trans. A*, 208, 381 (1908).

to continue to increase with increasing temperature until it attains the unusually high value of 0.74×10^{-8} at about 400° C. It remains approximately constant at this value until between 600° and 700° C. when it commences to decrease slightly.

§ II. ACKNOWLEDGMENTS

In conclusion the author desires to acknowledge his indebtedness to Dr G. W. C. Kaye, Superintendent of the Physics Department, for his encouraging interest in the work; to Dr F. H. Schofield for advice and assistance in the initial stages, and to Mr F. G. Filby and his successor Mr E. E. Smith, B.Sc., for assistance with the constructional and observational work.

APPENDIX

Experimental data for the thermal and electrical conductivity of a rod of nickel-plated Armco iron

Energy (W.)	Temperature (° C.)				$(t_2 - t_1) + (t_3 - t_4)$	$\frac{t_1 + t_2 + t_3 + t_4}{4}$ or T_S	$T_F - T_S^*$	Apparent thermal conductivity K_{TS}	True thermal conductivity	Electrical conductivity σ_{TS}
	t_1	t_2	t_3	t_4						
<i>First run</i>										
67.78	122.2	145.7	134.4	123.1	46.9	9.0				102,400
70.60	125.7	149.8	150.2	125.7	48.6	134.7	1.9	0.1578		
67.37	124.3	147.8	148.2	125.0	46.7	137.8	-1.2	0.1586		
						136.3	0.7	0.1575	0.1582	
67.92	165.0	190.1	190.5	166.4	49.2	136.3				
73.47	160.8	189.2	192.6	167.8	53.2	178.0	1.2	0.1507		
73.01	160.4	188.4	192.1	167.7	52.4	177.6	-1.1	0.1508		50,420
						177.1	-0.4	0.1522		
73.59	170.0	197.1	198.5	172.2	53.4	177.6			0.1512	
73.69	171.6	198.4	199.0	172.7	53.1	185.0	-0.2	0.1505		
73.32	170.7	197.8	199.1	172.8	53.4	185.4	-1.0	0.1515		
68.30	172.5	196.7	195.0	169.7	49.5	185.1	0.2	0.1500		
70.87	167.1	193.6	195.2	170.1	51.6	183.5	1.3	0.1507		
74.68	181.0	207.4	204.8	176.8	54.4	181.5	1.7	0.1500		
						192.5	-3.3	0.1499		
98.57	211.1	248.2	249.4	211.5	75.1	185.5			0.1505	
93.87	209.5	245.4	246.5	210.4	72.0	230.0	-2.6	0.1434		
94.43	208.9	244.5	245.9	209.5	72.0	228.0	-1.1	0.1424		
94.48	208.0	243.5	244.9	208.5	71.9	227.2	0.3	0.1433		
94.40	208.0	243.5	244.9	208.7	71.7	226.2	0.1	0.1434		
92.85	204.1	239.5	241.1	205.3	71.2	226.2	0.1	0.1437		
						222.5	0.1	0.1425		43,740
97.27	293.1	329.5	324.2	280.3	80.3	226.7			0.1433	
95.57	301.1	339.1	335.1	292.7	80.4	306.7	-6.4	0.1323		
91.37	311.5	351.2	352.1	315.0	76.8	317.0	-3.4	0.1298		
99.05	291.4	337.9	343.9	305.9	84.5	332.4	-4.6	0.1299		
109.82	299.4	350.2	355.7	313.0	93.5	319.8	0.4	0.1280		
						329.6	-7.8	0.1283		
						321.1			0.1283	
						432.0				22,300
106.7	464.1	509.6	503.2	439.2	109.1	479.1	0.7	0.1068		
106.0	463.2	508.4	501.9	438.8	108.3	478.1	-1.1	0.1069		
106.8	464.2	510.2	499.0	436.9	108.1	477.5	3.1	0.1079		
105.4	462.5	508.3	497.0	435.2	107.7	475.7	-1.1	0.1069		
104.8	454.7	498.4	493.0	430.9	105.8	475.7	1.2	0.1081		19,840
						469.2			0.1071	
						475.9				16,570
						548.6				
122.4	582.2	644.7	640.8	560.8	142.5	607.1	3.5	0.0938	0.0944	
						601.5				14,740
						200.3				44,340

* Difference between effective mean temperatures of furnace and specimen.

Energy (W.)	Temperature (° C.)				$(t_2 - t_1) + (t_3 - t_4)$	$t_1 + t_2 + t_3 + t_4$ or T_S	$T_F - T_S$	Apparent thermal conductivity K_{TS}	True thermal conductivity	Electrical conductivity σ_{TS}
	t_1	t_2	t_3	t_4						
Second run										
94.95	453.8	496.0	483.7	428.2	96.7	9.8 240.0 316.7 406.4 465.2 464.8 581.7 625.9 485.0 419.8 420.4 433.6 424.6 431.1	3.6	0.1072	0.1080	101,200 39,220 30,640 23,950 20,280 15,390 14,070 19,330
90.54	410.1	443.2	441.1	384.8	89.5	359.4	8.1	0.1105		
91.09	410.8	443.7	441.9	385.3	89.5	357.8	8.1	0.1111		
100.00	421.9	458.3	457.5	396.5	97.4	356.6 358.0 192.4 105.6	2.5	0.1121	0.1140	22,120
78.91	352.3	377.6	376.3	331.0	70.6	357.8	-1.9	0.1221		
78.18	350.8	376.2	374.4	329.7	70.1	356.6	2.7	0.1218		
76.29	349.6	374.6	373.0	329.0	69.0	358.0 192.4 105.6	3.7	0.1208	0.1220	27,210 46,620 65,440
Third run										
30.01	56.5	65.4	66.6	56.7	18.8	62.9 61.3	-1.9	0.1743		79,860
25.18	53.1	60.8	61.8	53.1	16.4	57.2	7.1	0.1672		
28.26	56.1	64.8	65.8	56.3	18.2	60.7	4.5	0.1695		
28.16	56.1	64.6	65.7	56.3	17.9	60.7	1.9	0.1717		
28.27	55.2	63.7	64.6	55.1	18.0	59.6	1.1	0.1710		
28.30	54.6	63.1	64.3	54.8	18.0	59.2 60.4	1.1	0.1717	0.1724	
69.74	107.2	129.3	132.2	108.5	45.8	119.3	-0.9	0.1661		
67.68	110.1	131.8	134.6	111.0	45.3	121.8	2.0	0.1631		
63.08	112.1	133.3	135.8	113.0	44.0	123.5	6.5	0.1565		
61.20	106.7	126.8	129.3	107.5	41.9	117.6	6.2	0.1595		
62.95	107.3	127.3	129.6	107.5	42.1	117.7	-2.2	0.1633		
62.6	107.2	127.3	129.6	107.5	42.2	117.4	-0.5	0.1620		
61.52	109.8	129.7	131.7	109.7	41.9	120.3 119.7	3.5	0.1608	0.1620	
76.09	197.7	223.8	223.6	191.6	58.1	209.2	7.2	0.1429		
75.19	208.3	234.8	236.0	205.7	56.8	221.2	-2.0	0.1445		
74.65	207.7	233.9	234.8	204.5	56.5	220.1	-1.4	0.1443		
74.37	207.4	234.5	237.4	208.7	55.8	222.0	-2.2	0.1453		
68.83	203.6	229.1	231.9	205.1	52.3	217.4 222.5 213.9 544.9	1.3	0.1438	0.1438	43,590 16,850
85.77	548.6	585.5	576.5	518.7	94.7	557.3	1.0	0.0989		
85.58	547.6	584.1	575.2	517.7	94.0	556.2	1.0	0.0994		
85.87	546.9	583.4	574.6	517.1	94.0	555.5	1.0	0.0998		
85.60	545.7	582.1	573.6	516.1	94.0	554.4 555.8 560.0 646.5 652.6 658.6 680.8 733.6 743.2 790.0 813.0 811.7 602.3 559.1 175.3	0.5	0.0994 ₅	0.0996	16,250 13,420 13,270 13,130 12,530 11,180 10,980 10,030 9,870 9,820 14,630 16,240 49,330

Energy (W.)	Temperature (° C.)				$(t_2 - t_1)$ + $(t_3 - t_4)$	$t_1 + t_2 + t_3 + t_4$ 4 or T_S	$T_F - T_S$	Apparent thermal conductivity K_{TS}	True thermal conductivity	Electrical conductivity σ_{TS}
	t_1	t_2	t_3	t_4						
Fourth run										
						15.3 198.8				96,800 45,660
73.78	220.2	247.9	250.8	223.2	55.3	235.5	-2.6	0.1457		
73.03	220.1	246.7	246.9	217.4	56.1	232.8	-0.1	0.1421		
73.32	219.9	246.2	246.3	216.9	55.7	232.3	0.0	0.1438		
72.75	226.6	254.4	256.1	227.0	56.9	241.0	1.4	0.1395		
73.06	226.2	253.5	254.7	225.8	56.2	240.0	1.5	0.1418		
72.19	226.2	253.6	254.6	225.9	56.1	240.1	1.1	0.1404		
72.52	225.9	253.2	253.8	225.1	56.0	239.5	2.4	0.1414		
						237.3			0.1425	
						551.6				16,190
76.17	561.2	593.9	585.6	534.1	84.2	568.7	-0.9	0.0988		
76.40	558.5	591.6	582.8	531.6	84.3	565.1	0.0	0.0990		
76.35	558.4	591.0	582.6	531.5	83.7	565.9	0.0	0.0996		
75.91	554.8	587.5	578.9	527.9	83.7	562.2	1.0	0.0990		
						565.5			0.0990	
75.85	627.4	663.6	656.5	603.0	89.7	634.6	0.0	0.0923	0.0923	
						643.0				13,520
75.10	695.7	737.4	729.4	669.5	101.6	708.0	2.8	0.0807		
73.80	689.5	729.7	722.5	666.6	96.1	702.1	2.9	0.0839		
74.08	686.8	727.8	722.0	667.1	95.9	700.9	2.3	0.0843		
						703.7			0.0845	
						700.8				12,040
						708.1				11,900
						771.4				10,270
76.75	753.7	807.2	804.1	746.3	111.3	777.8	1.3	0.0753		
81.45	746.6	799.4	795.6	735.8	112.6	769.3	2.1	0.0790		
81.22	748.5	801.4	798.4	735.4	113.9	771.4	0.3	0.0779		
85.01	760.4	817.1	813.3	747.3	122.7	784.5	2.4	0.0757		
						774.7			0.0776	
85.63	777.2	836.2	834.3	764.4	128.9	803.0	6.6	0.0726	0.0750	
						813.5				9,870
						792.0				10,050
						703.0				11,980
80.37	639.3	685.0	680.0	622.8	103.9	656.5	3.3	0.0844		
80.95	635.7	681.9	678.5	623.5	101.2	654.9	2.9	0.0874		
81.48	638.0	685.3	683.5	632.4	98.4	659.8	-1.4	0.0904		
						657.1			0.0890	
						665.9				12,930
						505.2				18,580
76.30	454.3	492.7	492.6	452.6	78.4	472.8	1.8	0.1063		
76.19	449.4	487.3	487.7	448.6	77.0	468.3	1.6	0.1080		
76.06	447.7	491.2	497.7	465.9	75.3	475.6	-2.5	0.1103		
75.50	459.3	504.6	510.9	477.7	78.5	461.2	4.5	0.1050		
						469.5			0.1086	
						307.4				31,840
						260.5				37,030
72.70	210.4	236.9	234.6	203.8	57.3	221.4	6.0	0.1385		
66.15	209.3	236.2	239.2	217.4	48.6	225.6	-3.0	0.1485		
65.04	204.6	229.8	230.6	207.2	48.6	218.0	1.6	0.1461		
64.10	204.4	229.8	230.5	206.7	49.2	217.8	1.3	0.1423		
61.36	215.2	236.5	236.4	213.3	44.4	214.2	-0.4	0.1484		
56.50	208.6	230.5	230.8	208.7	44.0	219.6	3.2	0.1402		
55.77	207.7	229.2	229.5	207.8	43.2	218.5	2.3	0.1410		
						219.3			0.1450	
						117.3				63,330
						14.0				100,800

Alternative method in which energy was measured by means of a water-flow calorimeter

Nickel-plated rod of Armco iron

Energy (cal.)	Temperature (° C.)			$\frac{1}{2}(t_1+t_2)$ or T_s	$T_F - T_s$	Apparent thermal conduc- tivity K_{TS}	True thermal conduc- tivity
	t_1	t_2	$t_1 - t_2$				
3.85	32.9 ₇	22.6 ₁	10.3 ₈	27.7	2.0	0.1701	
4.32	34.6 ₂	23.3 ₃	11.2 ₉	29.0	— 0.2	0.1749	
4.51	35.9 ₁	24.0 ₈	11.8 ₅	30.0	1.4	0.1739	
4.23	34.8 ₈	23.6 ₇	11.2 ₁	29.1	— 0.9	0.1724	
4.30	35.2 ₈	23.8 ₈	11.4 ₀	29.5	— 0.9	0.1724	
				29.1			0.1744
8.09	54.8 ₄	33.3 ₀	21.5 ₄	44.1	— 0.9	0.1717	
8.33	55.6 ₂	33.8 ₃	21.7 ₉	44.7	0.3	0.1746	
				44.4			0.1736
11.05	70.6 ₈	40.9 ₀	29.7 ₈	55.8	0.4	0.1697	
11.34	71.3 ₇	41.3 ₄	30.0 ₃	56.4	0.5	0.1725	
				56.1			0.1707
20.63	122.5 ₃	65.7 ₂	56.8 ₁	94.1	7.2	0.1659	
22.00	127.8 ₈	66.2 ₀	61.6 ₈	97.0	0.7	0.1631	
21.75	126.4 ₉	65.8 ₈	60.6 ₁	96.2	1.4	0.1640	
21.57	125.9 ₅	66.1 ₂	59.8 ₃	96.0	0.0	0.1647	
22.17	129.3 ₇	67.8 ₉	61.4 ₈	98.6	1.0	0.1648	
22.28	130.9 ₉	68.9 ₂	62.0 ₇	99.9	0.5	0.1640	
				97.0			0.1640
31.79	189.7	96.9	92.8	143.3	— 2.85	0.1565	
32.94	196.7	100.1	96.6	148.4	— 6.9	0.1558	
33.65	197.0	99.3	97.7	148.2	7.1	0.1574	
32.74	191.6	97.2	94.4	143.0	4.0	0.1584	
34.62	203.3	101.9	101.4	152.6	— 2.0	0.1560	
				147.1			0.1569
47.20	284.7	137.3	147.4	211.0	1.8	0.1463	
48.46	287.0	139.0	148.0	213.0	24.0	0.1496	
46.75	284.5	137.3	147.2	210.9	— 16.0	0.1451	
45.97	280.8	135.3	145.5	208.1	— 13.5	0.1443	
46.16	281.8	136.6	145.2	209.2	— 4.5	0.1452	
				210.4			0.1460

Unplated rod of Armco iron

Diameter, 7.345 cm.; distance between temperature points, 19.4 cm.

Energy (cal.)	Temperature (° C.)			$\frac{1}{2}(t_1+t_2)$ or T_s	$T_F - T_s$	Apparent thermal conduc- tivity K_{TS}	True thermal conduc- tivity
	t_1	t_2	$t_1 - t_2$				
7.82	59.2	37.8	21.4	48.5	— 2.15	0.1696	
8.22	61.1	38.7	22.4	49.9	— 1.7	0.1682	
8.14	59.9	38.3	21.6	49.5	4.9	0.1727	
8.54	62.0	38.9	23.1	50.5	1.1	0.1688	
8.40	59.2	36.4	22.8	47.8	— 1.0	0.1701	
8.66	59.9	36.7	23.2	48.3	— 0.9	0.1708	
8.62	60.0	36.7	23.3	48.3	— 1.2	0.1692	
8.22	57.8	35.8	22.0	46.8	0.1	0.1712	
				48.6			0.1710
15.94	98.4	54.5	43.9	76.4	— 3.2	0.1662	
15.86	97.6	54.0	43.6	75.8	— 2.5	0.1664	
16.04	98.2	54.3	43.9	76.2	— 2.0	0.1671	
14.98	91.8	51.6	40.2	71.7	4.2	0.1707	
15.21	92.6	52.1	40.5	72.4	4.4	0.1718	
14.42	90.3	50.8	39.5	70.5	— 1.3	0.1676	
14.51	89.9	50.4	39.5	70.1	— 1.3	0.1683	
14.47	90.4	50.8	39.6	70.6	— 0.9	0.1672	
				73.0			0.1684
24.75	150.2	79.9	70.3	115.0	— 1.3	0.1612	
27.68	168.2	88.1	80.1	128.2	— 3.5	0.1582	
				121.6			0.1604

DISCUSSION

Dr D. OWEN said that the curve in figure 3 seemed to be linear at its ends but not in the middle. Some change appeared to take place between 400 and 500° C. The electric curve, figure 4, showed no discontinuity, however. Were similar results obtained with all specimens?

Dr L. F. BATES. I should like to ask whether any changes in the resistance due to the ferromagnetic properties of the iron were observed. I should have expected a break in the curve of conductivity with temperature, in the neighbourhood of 750° C., but perhaps the scale does not permit this to be seen. It is well known that the resistance of a ferromagnetic metal is less than that of a normal metal by a term which is proportional to the intrinsic or spontaneous magnetization. This behaviour is well established in the case of nickel and I should expect to see evidence of it here.

AUTHOR'S reply. I agree with Dr Owen that there is a slight change in the slope of the thermal-conductivity, temperature curve for iron at about 400° C., although the magnitude of the change is only about half of that shown in figure 3 where the effect is exaggerated by the presence of the nickel plating.

In reply to Dr Bates: the resistance, temperature curve is typical of that of a ferromagnetic metal at temperatures below the critical point, and I hope to deal with both the thermal and electrical conductivity changes which occur within and above the critical region in a later communication.

THE CONDUCTIVITY OF METALS

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ABSTRACT. If the resistances of the pure metals are measured for the same amplitude of thermal oscillation of the atoms they show a marked periodic behaviour, being always two or three times greater for a monovalent element than for the divalent metal next to it in the periodic table. This fact is discussed on the basis of wave mechanics, and it is suggested that the periodic variation is due to a smaller effective number of free electrons in the divalent metals. Evidence in support of this view can be obtained from the optical constants of metals (§ 3) and from the increase of resistance due to foreign metals in solid solution (§ 4).

Bridgman's measurements of the change of resistance under pressure are discussed on the basis of wave mechanics (§ 5). In §§ 6 and 7 a quantitative theory is given of the behaviour under pressure of alloys and of pure metals at low temperatures, and in § 8 a qualitative explanation is given for the abnormal metals Ca and Sr, whose resistance increases under pressure.

§ 1. INTRODUCTION

IN this paper we shall discuss the electrical resistance of pure metals with reference to their place in the periodic table; we shall show how the observed increase of resistance due to foreign metals in solid solution leads to a better understanding of the factors affecting the resistance of the pure metals. We shall discuss also the change of resistance of metals and alloys under pressure, both at high and low temperatures, and show that the behaviour of both normal and abnormal metals can be accounted for qualitatively, and in some cases quantitatively.

It has been known since about 1910 that the electrical resistance of a pure metal depends in some way on the thermal motion of its constituent atoms. Kammerlingh Onnes*, Nernst† and Lindemann‡, for instance, remarked that, both in the region of high and low temperatures, i.e. above and below the Debye characteristic temperature Θ , the resistance of a given pure metal was approximately proportional to its thermal energy. To account for this fact, Wien§ in 1913 developed a theory of electronic conduction, in which the mean free path of an electron was *assumed* to be inversely proportional to the square of the mean thermal displacement of the ions. Grüneisen||, moreover, was able to account qualitatively on the basis of Wien's assumptions for the change of resistance of many metals under pressure.

* *Comm. Leiden*, 119 B, 1 (1911).

† *Berlin. Ber.* (1911) 316.

‡ *Verh. d. d. phys. Ges.* 15, 186 (1913).

§ *Berlin. Ber.* (1911) 306.

§ *Berlin. Ber.* (1913) 184.

The application of quantum mechanics to the problem by Bloch and others has provided a theoretical justification of Wien's assumption about the mean free path. The argument is as follows. An electron wave can pass quite freely through a perfect lattice, which therefore has infinite conductivity. A finite resistance only arises because, owing to the thermal motion of the ions or to the presence of impurities, the lattice is not perfect. At temperatures T greater than the characteristic temperature Θ , when there is no correlation between the thermal motion of one ion and that of its neighbour, one may calculate as follows the way in which the conductivity depends on temperature. If an ion is displaced from its mean position through a distance x , the amplitude of the incoherently scattered electron wave is proportional to x , and its intensity to x^2 . Clearly the resistance will be proportional to the mean square of the atomic displacement, which we shall denote by $\overline{x^2}$. Now if μx is the restoring force on a displaced ion, $\frac{1}{2}\mu x^2$ is the mean value of the potential energy corresponding to a displacement in the x direction, and may thus be equated to $\frac{1}{2}kT$. We have therefore

$$\overline{x^2} = kT/\mu.$$

But if ν is the atomic frequency, $4\pi^2\nu^2 = \mu/M$, where M is the mass of an ion. Since $h\nu = k\Theta$ we have, therefore,

$$\overline{x^2} = \frac{h^2}{4\pi^2k} \frac{T}{M\Theta^2} \quad \dots\dots(1).$$

To discuss the conductivity further, it is convenient to separate out the various factors as follows. Let us suppose that a metal contains N atoms per unit volume and that the current that would be produced in time δt by a field E , if there were no resistance, is

$$\frac{Ne^2}{m} f E \delta t.$$

The pure number f is equal to unity for a monovalent metal, two for a divalent metal, etc., only if the electrons are quite free—i.e. if the field of the ions is negligible. According to wave mechanics, for most real metals it is rather less than unity.

We write for the conductivity σ ,

$$\sigma = \frac{Ne^2}{m} f \cdot \tau.$$

The quantity τ is thus the time of relaxation of the current. For a good conductor such as silver the quantity τ is of the order of magnitude of

$$\frac{10^{-2} \text{ cm.}}{c} \text{ or } 3 \times 10^{-13} \text{ sec.}$$

τ is of course proportional to $\overline{x^2}$, so that

$$\tau \propto M\Theta^2/T.$$

f , on the other hand, is independent of T and of Θ .

§ 2. CONDUCTIVITIES OF PURE METALS

In table 1 are shown the measured values of the conductivities of some metals at 0° C. divided by $M\Theta^2$. The values given in column 4 therefore represent the conductivities of the metals for a value of the atomic displacement x which is the same for all the metals shown. The periodic nature of the series of values obtained is striking, in particular the large values for the alkalis and noble metals, the drop by a factor varying from 2 to 4 on passing to the divalent and trivalent metals, and the low values for the transition elements such as Fe, Ni, Pt. A periodic behaviour of this type has already been noticed by Grüneisen*, who plotted against the atomic number rather a different quantity, namely the conductivity measured at a temperature equal to $\frac{1}{2}\Theta$.

Now it is improbable that the scattering-power of an ion for given displacement—i.e. C in Bethe's equation (2) given below—and hence the mean free path will vary very much for two adjacent elements, although it is almost certainly very different for, say, K and Ag. It follows that the time of relaxation τ for given atomic displacement will vary smoothly from atom to atom, and thus that the periodic behaviour shown in table 1 is not due to τ .

It is further obvious that the periodicity in the conductivity is not simply determined by the atomic volume, since Lothar Meyer's well-known curve, in which atomic volume is plotted against atomic number, shows strong maxima for the alkali metals but no maxima at all for Cu, Ag and Au. We must therefore attribute the periodic behaviour of the conductivities to f , i.e. the factor which determines to what extent the electrons in a metal are free. The fact that f should be less for a divalent than for a monovalent metal is of course a fairly obvious consequence of the Bloch-Brillouin theory of metals, as has been realized for some time†.

One of the objects of this paper is to discuss methods by which f may be measured independently of τ (§§ 3 and 4). We shall first, however, discuss the probable values of τ from the point of view of wave mechanics.

In Bloch's treatment the state of each electron is defined by a wave function of the type

$$\psi = e^{i(\mathbf{K}\mathbf{r})} \psi_{\mathbf{K}}(x, y, z),$$

with energy $W(\mathbf{K})$. The conductivity has only been treated for the case in which W is a function of the modulus K of \mathbf{K} ; in this case Bethe‡ gives the following formula for the conductivity

$$\sigma = \frac{1}{\pi^3} n e^2 \left(\frac{K}{C} \frac{dW}{dK} \right)^2 \frac{2\pi k}{\hbar K a_0} \frac{\Theta^2}{T} \frac{M}{m} \quad \dots\dots(2),$$

where n is the number of electrons per atom and a_0 the radius of a hydrogen atom, K , dW/dK refer to the maximum energy of the Fermi distribution, and C is a

* *Handb. d. Phys.* 10, chap. 1.

† Cf. for example, Brillouin, *Die Quantenstatistik*, 313 (Berlin 1931).

‡ *Handb. d. Phys.* 24-2, 521 (1933).

Table I.

	1 M	2 Θ^*	3 σ^\dagger	4 $\sigma/M\Theta^2$ (arbitrary units)
Li	7	510	11.8	0.65
Be	9	1000	18	0.20
B	10.8	(1200)	—	—
Na	23	172	23.8	3.5
Mg	24	290	25	1.25
Al	27	396	40	1.0
K	39	126	15.9	2.6
Ca	40	226	23.5	1.12
Cr	52	485	6.5	0.053
Mn	55	(330)	—	—
Fe	56	453	11.2	0.1
Co	59	385	19	0.22
Ni	59	375	16.1	0.20
Cu	64	310	64.5	1.05
Zn	65	235	18.1	0.52
Rb	85	(85)	8.6	1.4
Sr	88	(140)	3.3	(0.2)
Mo	96	379	20	0.146
Rh	102	370	22	0.158
Pd	107	(230)	10.3	0.237
Ag	108	215	66.7	1.32
Cd	112	168	14.7	0.47
In	115	—	11.9	—
Sn	119	—	9.9	—
Cs	133	(68)	5.6	0.92
Ba	137	(110)	—	—
Ta	181	245	—	—
W	184	320	20.4	0.10
Ir	193	285	20.0	0.13
Pt	195	225	10.2	0.105
Au	197	175	49.0	0.82
Hg	201	97	4.4	0.23
Tl	204	96	7.1	0.37
Pb	207	90	5.2	0.30
Bi	209	110	1.3	0.051

* Θ is the characteristic temperature. The unbracketed values are taken from Landolt-Bornstein's *Tables*, 2^{te} *Ergänzungsband*, 1232, and from R. H. Fowler, *Statistical Mechanics*. The bracketed values are estimated from the compressibility, etc.

† σ is the conductivity in $\text{cm}^{-1}\Omega^{-1}$ at 0°C . Most of the values are taken from Grüneisen, *Handb. d. Phys.* 13, 11.

quantity depending on the size of the metallic ion, but not on the structure of the crystal. It may further be shown that*

$$\frac{Ne^2}{m} f = nNe^2 \frac{4\pi^2}{Kh^2} \frac{dW}{dK} \quad \dots\dots(3).$$

For free electrons, for which $W = h^2 K^2 / 8\pi^2 m$, this reduces to $f = n$.

We obtain for the time of relaxation, dividing (2) by (3),

$$\tau = \text{constant} \times \frac{1}{N} K^2 \frac{dW}{dK} \frac{M\Theta^2}{T}.$$

For free electrons $N \propto K^2$, and in general it is probable that the error is not serious if we write

$$\tau = \text{constant} \times \frac{dW}{dK} \frac{M\Theta^2}{T} \quad \dots\dots(4).$$

For divalent metals, where the first Brillouin zone is nearly full, the assumption that W is a function only of K is certainly false, and equation (2) cannot be applied. An exact expression may however be given for f as follows. The acceleration of an electron in the state defined by \mathbf{K} due to a field F in the x direction is

$$\ddot{x} = eF \frac{\partial^2 W}{\partial K_x^2} \frac{4\pi^2 m}{h^2}.$$

If N be the number of atoms per unit volume, then

$$\frac{Ne^2}{m} f = \frac{4\pi^2 e^2 m}{h^2} \frac{2N}{V} \iiint \frac{\partial^2 W}{\partial K_x^2} dK_x dK_y dK_z.$$

It is easily seen that, if W is a function of K only, this formula reduces to (3), since in this case $2N/V = \frac{4\pi}{3} K_{\text{max}}^3$.

The formula may easily be transformed to

$$\frac{Ne^2}{m} f = \frac{4\pi^2 e^2 m}{h^2} \frac{2N}{V} \iiint \frac{1}{|\text{grad } W|} \left(\frac{\partial W}{\partial K_x} \right)^2 dS \quad \dots\dots(5),$$

integrated over the surface of the Fermi distribution. The smallness of this quantity for divalent metals is due to two causes. (1) Over a large part of the surface $\partial W / \partial K_x = 0$. Thus in figure 1 $\partial W / \partial K_x$ vanishes along AB and along CD , showing that the part of the Fermi distribution within $ABB'A'$, $CDD'C'$ is not displaced at all under the action of the field. (2) Even on parts of the surface BC , etc., $\partial W / \partial K$ is smaller than it would be for free electrons, or for a monovalent metal, especially near to B and C . H. Jones†, however, has shown that dW/dK will have, over most of the surface BC , a value nearly equal to its free electron value. The first effect, therefore, is the more important.

For divalent metals, although no exact theory of τ can be given at present, we shall assume that a fair estimate can be made by using formula (4) and by averaging dW/dK over that part of the surface of the Fermi distribution for which it does not vanish, because it is only between such points that electronic transitions can take

* See equation (5) below.

† *Proc. R.S.* (in the press).

place. Since, as we have said, dW/dK has very nearly its free-electron value over these parts of the surface, we shall be fairly safe in assuming that τ will be nearly the same for a monovalent and a divalent element which are near together in the periodic table, for given atomic displacement. *Thus we may assume that, for the values of $\sigma/M\Theta^2$ in the last column of table 1, the time of relaxation τ is a fairly smooth function of atomic number.*

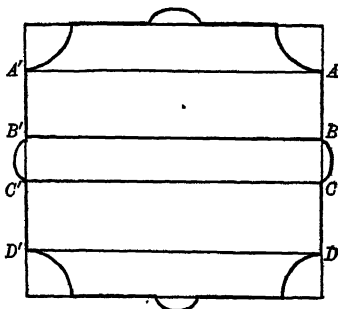


Figure 1. The Fermi surface for a divalent metal.

§ 3. OPTICAL METHODS OF DETERMINING f

The quantity f may in principle be determined by optical methods for any good conductor. If light falls on a metal, and if the period ν^{-1} of the light is small compared with the time of relaxation τ , then the current set up by the electric field of the light wave is approximately independent of τ . If the absorption of energy may be neglected altogether, so that $\tau = \infty$, the complex refractive index \mathbf{n} of the metal is given by

$$\mathbf{n}^2 = 1 - \frac{Ne^2f}{\pi m \nu^2}.$$

For frequencies in the visible region \mathbf{n} is usually imaginary and equal to $i\kappa$, say. Thus f may be deduced if the extinction coefficient κ is measured. Unfortunately, for wave-lengths in the visible, bound electrons may have some effect on the absorption coefficient; the best way to determine f is to plot the quantity

$$\frac{(1 - \mathbf{n}^2) \pi m \nu^2}{Ne^2} \text{ or } f$$

against ν . If the values of f obtained are not independent of ν , one must extrapolate to zero frequency, or rather to the lowest frequencies consistent with the condition $\nu^{-1} \ll \tau$.

By this method, Dr Zener and the present author have obtained* the following values of f :

Metal	Li	Na	K	Rb	Ag	Au	Ni	Pt
f	0.6	1.0	0.8	0.7	1.0	0.7	0.18	0.42

* *Proc. Camb. Phil. Soc.* 30, 262, table 1 (1934). In that paper N' is written for our Nf . The values for Ni and Pt are very uncertain, and the others are unlikely to be correct to more than 10 per cent.

§ 4. RESISTANCE OF ALLOYS

The quantity f , the free electron number, may also be determined from experiments on the resistance of alloys. If an alloy is formed in which, say, 1 per cent of a metal B is in solid solution in a metal A , then, provided that the structure is not changed, the resistance of the alloy is always higher than that of the pure metal A . If ΔR is the difference between the specific resistance of the alloy and that of the pure metal, ΔR is found to be approximately independent of temperature, according to Matthiessen's rule. According to Nordheim*, the explanation is as follows. The field of the foreign atom B is different from that of the solvent metal A ; thus extra scattering-power is caused by the difference between the fields, the extra resistance ΔR being proportional to a term of the type

$$\iiint [V_A(r) - V_B(r)]^2 dx dy dz \quad \dots\dots(6),$$

V_A and V_B being the potentials of an electron in the field of an ion of the metal A or of the metal B . Nordheim's theory does not take into account the actual distortion of the lattice by the foreign atom, and this distortion may in fact lead to a further increase in the resistance. We shall however neglect it.

For our purpose it is important to note that a term of the type (6) is symmetrical with respect to A and B ; in other words, other things being equal, one atomic per cent of a metal A dissolved in B will produce the same increase of resistance as one atomic per cent of B in A . This is in fact the case for such pairs of metals as (Mg, Cd), (Cu, Au) and (Pt, Pd), as table 2 shows†.

Table 2. Change of specific resistance ΔR ($\mu\Omega/\text{cm}^2$).

Cu in Au	0.74	Au in Cu	0.6 to 0.64
Mg in Cd	0.4 to 0.45	Cd in Mg	0.5 to 0.6
Pt in Pd	0.7	Pd in Pt	0.55 to 0.6
Ag in Au	0.3 to 0.36	Au in Ag	0.3
Cu in Ag	0.4 to 0.5	Ag in Cu	0.22?

In all these cases, except Cu, Ag, the atomic volumes do not differ by more than 20 per cent.

On the other hand, if N' (i.e. Nf), the effective number of free electrons per unit volume, is not the same for a pair of metals, this will no longer be the case. To see that this is so, let us take the case of Ag and Mg. At very low temperatures the resistance ΔR will be the whole resistance of the alloy, by Matthiessen's rule. Let τ be the time of relaxation, at such temperatures, either for 1 per cent of Ag

* *Ann. d. Physik.* 9, 641 (1931); cf. also Bethe, *Handb. d. Phys.*, loc. cit. These calculations depend also on the assumption that W is a function of K only; but the conclusions are probably valid under the conditions stated at the end of § 2.

† Norbury, *Trans. Far. Soc.* 16, 570 (1921).

in Mg or 1 per cent of Mg in Ag; from what has been said above it follows that the two are equal. Then for conductivity at low temperatures we have

$$1/\Delta R \propto N'_{\text{Ag}}\tau \text{ for Mg in Ag;}$$

$$1/\Delta R \propto N'_{\text{Mg}}\tau \text{ for Ag in Mg,}$$

where N'_{Ag} , N'_{Mg} are the numbers of electrons per unit volumes in the two metals.

Now in fact for these two alloys we find the following values*:

$$\Delta R$$

$$\Delta R$$

1 per cent Mg in Ag, 0.8 to 1.3;

1 per cent Ag in Mg, 3 to 3.5

and again the atomic volumes are nearly equal. We therefore deduce that the free-electron number per unit volume, f , in silver is about three times as great as for magnesium.

Another case is that of gold and cadmium*; for these the values are

1 per cent Cd in Au, 0.64 (0.35†);

1 per cent Au in Cd, 1.7 to 1.9.

In this case also the atomic volumes are almost the same.

These values, then, confirm our hypothesis that f for any monovalent metal is three or four times greater than for any divalent metal. Probably for monovalent metals the values lie between 0.7 and 1, and for divalent metals from 0.2 to 0.4, in spite of the presence of two electrons.

It is interesting to note that the two metals considered above, Ag and Mg, have about the same corrected conductivity in table 1; this must be due to the small scattering power C , equation (2), of a small ion, such as Mg, in comparison with that of a large ion, such as Ag.

Further experimental data on the change of resistance due to foreign metals in solid solution would be very interesting.

§ 5. CHANGE OF RESISTANCE UNDER PRESSURE

Bridgman† has found that the resistance of most metals decreases under pressure, but that for certain metals (Li, Ca, Sr, Bi) it increases. The decrease of resistance of the normal metals has been explained by Grüneisen§ in the following way. The atoms of a metal under high pressure, being closer together, are held in their positions by stronger forces, and therefore vibrate with higher frequency, than at atmospheric pressure. The atomic vibrations at given temperature are therefore smaller, and the resistance is therefore lower. If dv/dp denotes the rate of change of atomic frequency with pressure, then, since by equation (1) the resistance is inversely proportional to the square of the frequency, we shall have

$$\frac{1}{R} \frac{dR}{dp} = -2 \frac{1}{\nu} \frac{d\nu}{dp} \quad \dots\dots(7).$$

Grüneisen has shown how dv/dp may be calculated from the thermal expansion coefficient, and has thus been able to compare formula (7) with the results of

* Norbury, *loc. cit.*

† *The Physics of High Pressures* (1931).

‡ Earlier measurement.

§ *Verh. d. d. phys. Ges.* 15, 186 (1913).

experiment. In table 3 we give the change of conductivity with volume obtained by dividing Bridgman's values of the pressure coefficient of resistance by the compressibility, and compare them with $-2d(\log \nu)/d(\log V)$, which, according to Grüneisen*, may be calculated from the formula

$$\frac{\alpha(\log \nu)}{d(\log V)} = -\frac{\alpha V}{\chi c_v},$$

Table 3.

Element	$-2 \frac{d(\log \nu)}{d(\log V)}$ (Grüneisen)*	$-\frac{d(\log \sigma)}{d(\log V)}$ (Bridgman)	Element	$-2 \frac{d(\log \nu)}{d(\log V)}$ (Grüneisen)*	$-\frac{d(\log \sigma)}{d(\log V)}$ (Bridgman)
Li	2.34	-0.85	Mo	3.14	3.7
Na	2.50	2.84	W	3.24	4.3
K	2.68	4.0	Mn	4.84	8.3†
Rb	2.96	2.92	Fe	3.20	4.1
Cs	2.58	1.8	Co	3.74	1.76
Cu	3.92	2.7	Ni	3.76	3.35
Ag	4.80	3.6	Pd	4.46	3.75
Au	6.06	5.2	Pt	5.08	5.6
Al	4.34	2.9	Ca	—	-1.95
Pb	5.46	6.0	Sr	—	-6.7
Ta	3.50	2.9	Ba	—	+0.58

* *Loc. cit.*

† Not pure.

where α is the thermal expansion coefficient, c_v the specific heat and χ the compressibility. Only cubic metals are shown in the table. One sees that there is rather good agreement as regards the order of magnitude of the effect for many metals, but that the increase of conductivity is in general rather less than the predicted increase. In Cu, Sr and Li it is very much less, being converted into a decrease.

When the difference between the columns of table 3 is small, it may perhaps be attributed only to the change in the number of atoms per unit volume which results from compressing the metal; in many cases, however, it must be attributed to a variation in the effective number of free electrons per atom, i.e. to a change in f . The reason for the large decrease in Sr will be discussed below; we shall first adumbrate some consequences of this hypothesis.

§ 6. RESISTANCE OF ALLOYS UNDER PRESSURE

According to Matthiessen's rule, the extra resistance ΔR produced by a given percentage of a foreign metal such as gold in solid solution in, say, silver, is independent of temperature. From Grüneisen's theory of the pressure coefficient, it would follow that ΔR , which depends on the difference in scattering power of the two atoms, should be independent also of pressure, if, and only if, the change of resistance is entirely due to a change in ν . Thus for Cu, Ag and Au, containing foreign atoms in solid solution, one would expect ΔR to be independent of pressure, because for these metals, as table 3 shows, the change of resistance is almost entirely

* *Handb. d. Phys.* 10, 28 (1928).

due to the change in ν . On the other hand, for lithium the effective number of free electrons must decrease under pressure, and hence the change of resistance ΔR due to foreign atoms dissolved in Li will increase under pressure, and will indeed increase more than the resistance of the normal metal; one would expect that for Li

$$\frac{d(\log \Delta R)}{d(\log V)} = -3.2,$$

the number -3.2 being the difference between the two values in table 3. Experimental evidence to test this hypothesis is not at present available, but Bridgman states that the pressure coefficient of alloys is in general less than for pure metals, as we should expect.

§ 7. PRESSURE COEFFICIENT AT LOW TEMPERATURES

At low temperatures, such that $T < \Theta$, the equation (1), $R \propto T/\Theta^2$, is no longer true; the exact formula for the conductivity due to Bloch* is

$$R = \frac{1}{\sigma} = \frac{A}{\Theta} \left(\frac{T}{\Theta} \right)^5 J \left(\frac{\Theta}{T} \right) \quad \dots\dots(8),$$

where the function J is defined thus

$$J = \int_0^{\Theta/T} \frac{x^3 dx}{(e^x - 1)(1 - e^{-x})}$$

and A is independent of T and Θ , but depends on the crystal structure, etc.

The function J tends to a constant value as $T \rightarrow 0$, and is proportional to $(\Theta/T)^4$ for high temperatures. It follows that, for the rate of change of conductivity with Θ , we have

$$\frac{d(\log \sigma)}{d(\log \Theta)} = \left\{ \frac{\Theta}{J} \frac{dJ}{d(\Theta/T)} - 6 \right\}.$$

This quantity may be calculated from values given by Bethe* and shown in table 4.

Table 4.

Θ/T	0	1	2	3	4	5	8	∞
$-\frac{d(\log \sigma)}{d(\log \Theta)}$	2	2.2	2.4	2.85	3.35	3.9	5.1	6

Since the change in Θ resulting from a given pressure will be approximately the same at any temperature, we should expect, for pure metals, that the pressure coefficient of resistance would increase at low temperatures; that part of it which is due to the change in Θ will be given by

$$\frac{d(\log \sigma)}{d(\log V)} = \frac{d(\log \sigma)}{d(\log \Theta)} \frac{d(\log \Theta)}{d(\log V)}.$$

That part of the pressure-change which is due to an increase in the number of free electrons, and hence of A in equation (8), will however be independent of

* Bethe, *Handb. d. Phys.* 24, (2), 532 (1933).

temperature, and may thus be found by subtracting the two columns of table 3. Denoting this term by $d(\log A)/d(\log V)$ we have for the pressure coefficient of resistance at any temperature

$$\frac{d(\log \sigma)}{d(\log V)} = \frac{d(\log A)}{d(\log V)} + \frac{d(\log \sigma)}{d(\log \Theta)} \cdot \frac{d(\log \Theta)}{d(\log V)}.$$

From this formula, the pressure coefficient of resistance of a metal at any temperature T may be calculated, if the pressure coefficient at room temperature is known.

Bridgman* has measured the pressure coefficient of a series of metals at 0°C . and at -182.9°C . Table 5 gives the ratio r of the pressure coefficient at -182.9°C . to that at 0°C . Column 1 gives the quantity $\frac{d(\log \sigma)}{d(\log \Theta)} \cdot \frac{d(\log \Theta)}{d(\log V)}$ at 0°C ., and column 2 at -182.9°C . Column 3 gives $\frac{d(\log A)}{d(\log V)}$, i.e. the change due to a variation in the free-electron number, obtained by subtracting columns 1 and 2 of table 3. Column 4 gives the calculated ratio r of the pressure coefficients, i.e. $(1+3)/(2+3)$, and column 5 gives the ratio of the two pressure coefficients as measured by Bridgman. The metals are arranged in the order of increasing Θ .

Table 5.

	Θ	1	2	3	r theoretical	r experimental
Pb	90	5.5	5.75	0.5	1.04	1.0
Au	175	6.2	7.1	-0.9	1.17	1.1
Ag	215	5.0	6.2	-1.2	1.32	1.2
Pt	225	5.3	6.6	0.5	1.22	1.2
Pd	230	4.7	5.8	-0.7	1.28	1.32
Cu	310	4.2	6.0	-1.2	1.60	1.65
Ni	375	4.1	6.5	-0.4	1.64	1.0
Mo	379	3.4	5.4	0.6	1.51	1.45
Al	396	4.8	7.9	-1.44	1.93	2.13

Except for nickel the agreement is excellent. For the metals Fe, Ta and W (not shown in the table), however, the measured coefficients at -182.9°C . were equal to or slightly less than those at 0°C ., although the theoretical values of r are 1.6, 1.3 and 1.5 respectively. This is almost certainly due to the *Restwiderstand* of the metal. If the metal is impure and has a *Restwiderstand* ρ_1 independent of pressure, the measured pressure coefficient will be

$$\frac{1}{\rho + \rho_1} \frac{d\rho}{dP} \quad \dots\dots(9),$$

where ρ is the specific resistance of the pure metal. Bridgman in his paper gives values of ρ_{90}/ρ_{273} for the specimens used by him, and compares them with the values given in the *International Critical Tables* and repeated in table 6.

* *Proc. Amer. Acad. of Arts and Sci.* 67, 305 (1932).

Table 6.

ρ_{90}/ρ_{273}	Pb	Au	Ag	Pt	Pd	Cu	Ni	Mo	Al	Fe	Ta	W
Bridgman	·2985	·278	·250	·249	·234	·187	·177	·158	·152	·164	·416	·313
International Critical Tables	·2953	·270	·250	·246	·329	·189	·208	·230	·189	·120	·330	·195

It will be noticed that all these metals except Fe, Ta and W were as pure or purer than those of the *International Critical Tables*; but that in Fe, Ta and W at least a third of the measured resistance must have been of the nature of *Restwiderstand*. As formula (9) shows, a *Restwiderstand* of this order of magnitude would be enough to mask the increase of $\rho^{-1}d\rho/d\rho$ at low temperatures.

§ 8. THE METALS WITH ABNORMAL PRESSURE COEFFICIENT

The abnormal pressure coefficients of Ca and Sr are rather easily explained. These metals are divalent and cubic. For a cubic metal the first Brillouin zone contains just two electronic states per atom, so that if the energy-gap bounding it were sufficiently large there would be no overlap into the second zone, as in figure 1, and the metal would be an insulator. To explain the abnormal pressure coefficient we must show that when the metal is compressed the energy-gap may increase faster than the total breadth of the Fermi distribution, so that the overlap, and hence f , decreases.

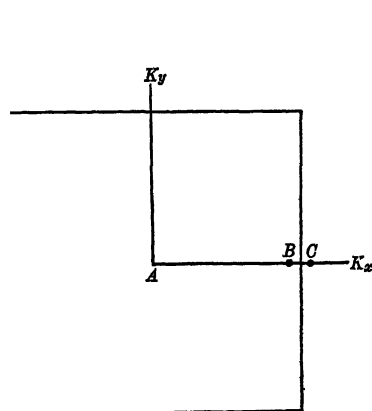


Figure 2a.

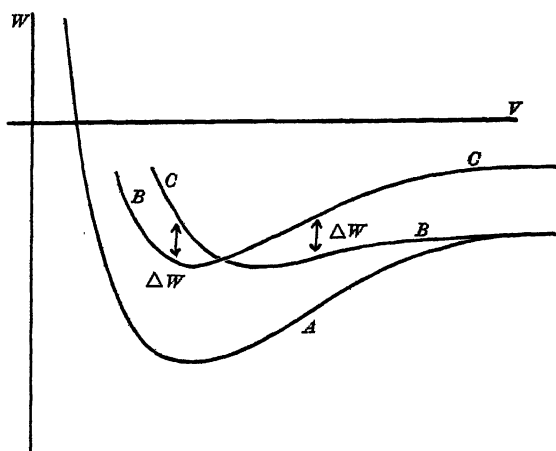


Figure 2b.

Figure 2a shows a section through the first Brillouin zone for a cubic crystal; A is the point with lowest energy, B is the point with lowest energy lying within the first zone just on a surface of energy-discontinuity, and C is the point of lowest energy in the second zone. The energy-difference between B and C is the energy-gap ΔW referred to above.

Now the wave functions corresponding to the points B and C will have nodes

either passing through the nuclei of the atoms (P functions) or mid-way between them (S functions); which of these wave functions corresponds to B , and which to C , depends on which has the lowest energy. The experiments of O'Bryan and Skinner* have shown that in magnesium the P wave functions have lower energy†, and this may well be the case also in Ca and Sr. On the other hand if one could increase the atomic volume indefinitely the energies of the S and P wave functions would tend respectively to the energy values of the lowest S and P states of the free atom. The energy of the S wave function will therefore, in the limit, be lowest. The energies of the states A , B , C will be as plotted in figure 2*b*. For some value of the volume V rather greater than the real volume of the crystal the curves B and C will cross, and ΔW will vanish.

We see, therefore, that ΔW will increase when the crystal is compressed, and that a small change of V may cause a large change in ΔW , as we require.

The discussion of non-cubic metals is more difficult, because there the pressure will change the c/a ratio as well as ΔW . It does not seem possible at present to make predictions about their behaviour. It is also difficult to explain the abnormal pressure coefficient of Li.

* *Phys. Rev.* **45**, 370 (1934).

† *Ibid.* **45**, 379 (1934).

THE PHOTOELECTRONS EXPELLED FROM ELEMENTS BY CHROMIUM K RADIATIONS

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ABSTRACT. Earlier work on the magnetic spectroscopy of X-ray electrons is extended by the use of X rays of longer wave-length than those previously employed. Groups of photoelectrons ejected from targets of gold, platinum, tungsten, samarium, lanthanum, tin, silver and copper by chromium K radiations have been photographed, and their energies are tabulated and compared with the values to be expected from X-ray data. The relative intensities of the groups and other details of their appearance are briefly discussed.

§ 1. INTRODUCTION

THE energies of the photoelectrons ejected from a number of elements by homogeneous X rays have already been measured in a great many cases. The present series, in which chromium K rays are employed as the primary X radiation, is an extension of earlier work in which the K radiations of copper^(1,2,3), molybdenum⁽⁴⁾ and silver⁽⁵⁾ were used. The details of the method are given in reference (1), and the apparatus now used is that described in reference (3).

Briefly, the experiments are carried out as follows. The primary X-ray beam passes through a slit, closed airtight by a very thin aluminium or cellophane window, into an evacuated camera, where it falls upon a target composed of a narrow strip of the element under examination. The apparatus is situated in an approximately uniform magnetic field, and some of the photoelectrons emitted by the target describe approximately circular paths in the camera. A fine wedge-shaped bundle of these photoelectrons, selected by a narrow slit, is bent round by the magnetic field so that it is received by a photographic plate. The bundle splits up into a number of separate beams, corresponding to groups of photoelectrons with different velocities; these beams are made, by the application of a well-known semi-circular focusing device, to register as sharp lines on the photographic plate. The positions of these lines yield the corresponding values of rH , where r is the radius of curvature of the path of an electron in a field H perpendicular to the plane of the path. The kinetic energy K of the electron is calculated from rH by the relativity formula, values of e and e/m_0 being assumed for the purpose.

According to the Einstein photoelectric equation, K should be equal to $h\nu_0 - W$, where W is the work required to extract the electron from the atom and ν_0 is the frequency of the primary X rays. W also = $h\nu_c$, where ν_c is a critical absorption

frequency of the element forming the target, or a frequency corresponding to a term in its X-ray spectrum, which is in most cases known from X-ray spectroscopy. The measurements therefore serve as a check both on X-ray data and on the values of the atomic constants⁽⁶⁾.

§ 2. DESCRIPTION OF TABLES IN § 3

The substances investigated in this series were gold (79), platinum (78), tungsten (74), samarium (62), lanthanum (57), tin (50), silver (47) and copper (29). With 74, 62 and 57 thin layers of oxide were used, in other cases the metal; tin and copper were used in the form of foils, and gold, platinum and silver as thin deposits on glass or aluminium.

The results are given in tables 1 to 8. To facilitate comparison with X-ray spectral data, the kinetic energies of the photoelectrons are converted into equivalent frequencies by Planck's relation, and then divided by the Rydberg frequency. These energies, thus expressed in the customary units of ν/R , are denoted by ν^*/R to distinguish them from the X-ray spectroscopic values.

In calculating ν^*/R from rH , I now take provisionally $e = 4.768 \times 10^{-10}$ e.s.u., $e/m_0 = 1.757 \times 10^7$ e.m.u. gm.⁻¹, and $h = 6.547 \times 10^{-27}$ erg.-sec. These differ appreciably from the values used in reference (3), especially for e/m_0 . There is however some authority for these revised figures, and it will be seen that they lead in many cases to an extraordinarily close agreement between the photoelectric results and the corresponding X-ray data.

The results tabulated for gold, tungsten, silver and copper may be compared with those given in reference (3)—bearing in mind that the rH values of Robinson, Andrews and Irons are all too high by approximately 0.08 per cent⁽⁷⁾; the ν^*/R values are all to be reduced by 0.16 per cent on this account, and by a further 0.22 per cent to make them correspond with the values of e , e/m_0 and h now adopted. The detailed comparison between the numerical values obtained in the two series is, however, deferred to a later paper, which will include additional results obtained with copper K radiation. In the present paper only the chromium K results will be considered.

In the following tables the intensity is given on a purely arbitrary scale, based only on visual estimates; 1 represents the weakest, 6 the strongest lines measured. All the photographs were taken on Schumann plates. As is well known, owing to the difficulty of accurately reproducing the extremely thin layer of emulsion, these plates tend to vary somewhat widely in sensitivity; with the Hilger Schumann plates used in the present work, it was found that although there were marked differences between different batches, very little trouble was caused by variations in sensitivity over any individual plate. The estimates of intensity are therefore not seriously vitiated by variations in the plates. On the other hand, in comparison with the plates most frequently used in the earlier work (Ilford X Ray and Process, Paget Half-Tone), the Schumann are relatively much more sensitive to slow electrons and less sensitive to swifter electrons. The relative intensities of the lines

due to the faster electron groups here recorded would have been possibly 1 or 2 units higher with the plates formerly used.

After the intensity, rH is given in gauss.-cm. then the energy ν^*/R in Rydberg units. The next column indicates the origin of the group of photoelectrons, or one or more possible origins. The fluorescent lines, representing photoelectrons of the second kind†, are indicated by the letter *F*. With each of these the assumed level of origin is accented in the tables, to emphasize the fact that here the photoelectron comes from an atom which is already ionized in one of its X-ray levels, and not, as is the case with the secondary cathode rays, from an atom which is initially in its normal state. The work of extraction will obviously be greater than from a normal atom, and further, as this work depends on the exact state in which the parent atom is left—i.e., on one of a great variety of possible modes of double ionization—the spectra of the fluorescent lines may be expected to be very complex. Both these expectations are realized, as may be seen from inspection of the tables, though the complexity of the fluorescent spectra is to some extent masked by the insufficiency of the resolving-power of the apparatus.

§ 3. RESULTS

In examining the tables, it is as well to remember that, as a result of the focusing method employed, the lines are in fact sharp only on their high-velocity edges, tailing off on the low-velocity side. With a close pair, then, the member of smaller energy may be obscured by the tail of its companion. Thus there are many instances where photoelectrons from the N v level can be easily measured, while those from N iv cannot be separated. Again, in other cases where resolution is just possible, there may be some doubt as to the intensity of the line of lower energy, although the position of the line may be measurable with considerable accuracy. There are many examples of this in the following tables.

The only constituents of the primary beam which need be quoted are

$$\text{Cr } K\alpha_1: \nu/R = 398\cdot8,$$

$$\text{Cr } K\beta_1: \nu/R = 438\cdot0.$$

The former of these, which is about five times as intense as the latter, is by far the more important in this work.

The X-ray data, both for levels and emission lines, have in general been taken from the last edition of Siegbahn's treatise, *Spektroskopie der Röntgenstrahlen* (1931), although in certain cases more recent data are available.

† See, in particular, references (4) and (5).

Table 1. 79, gold (metal)

Level-values, ν/R : M I	252.2	N I	55.8	O I	7.8
M II	231.8	N II	47.3	O II, III	4.1
M III	201.9	N III	39.9	O IV, V	0
M IV	168.6	N IV	25.8		
M V	162.2	N V	24.5		
		N VI	6.2		
		N VII	5.8		

Emission lines: $M\alpha_1$ 156.4; $M\beta$ 162.4; $M\gamma$ 177.5; (M II N IV) 206.0; (M I N II, III) 212.4

Remarks	Intensity	rH	ν^*/R	Origin
Not fully resolved	(?) 2	150.4 _s	146.5	M I : $CrK\alpha_1 - 252.3$
—	3	151.7	149.0	F : $AuM\alpha_1 - 7.4 (N', O')$; (M II N IV) - 57.0 (N')
—	2	154.9	155.3	F : $AuM\beta - 7.1 (N', O')$
—	3	160.7	167.1	M II : $CrK\alpha_1 - 231.7$
†	2	171.1	189.4	F : (M I O III) - 58.7 (N') ?
—	5	174.5	197.0	M III : $CrK\alpha_1 - 201.8$
†Weak: inaccurate	0-1	183.3	217.3	F : M I - (N' + N') or M II - (N' + O')
†Weak: inaccurate	i	186.0	223.7	F : M - (N' + N') or M - (N' + O')
—	6	188.7	230.3	M IV : $CrK\alpha_1 - 168.5$
—	6	191.3	236.6	M V : $CrK\alpha_1 - 162.2$
—	1-2	204.3	269.8	M IV : $CrK\beta_1 - 168.2$
—	1-2	206.7	276.1	M V : $CrK\beta_1 - 161.9$
—	2	230.7	343.7	N I : $CrK\alpha_1 - 55.1$
—	3	233.6	352.3	N II : $CrK\alpha_1 - 46.5$
—	4	236.0	359.6	N III : $CrK\alpha_1 - 39.2$
—	5	241.0	374.9	N IV, V : $CrK\alpha_1 - 23.9$
—	3	247.2	394.3	N VI, VII, O : $CrK\alpha_1 - 4.1$
—	1	248.9 _s	399.9	N III : $CrK\beta_1 - 38.1$
Narrow band	2	253.5	414.6	N IV, V : $CrK\beta_1 - 23.4$

† The hardest line recorded in the M emission spectrum of gold is (M I N III), with ν/R 212.4—(M I O III) has never been recorded. The two faint lines with $\nu^*/R = 217.3$ and 223.7 cannot be explained as due to internal conversion of a known X-ray line. They could however perfectly well arise, in more than one way, from internal rearrangements of the atom following M I or M II excitation.

Table 2. 78, platinum (metal)

Level-values, ν/R : M I	242.0	N I	52.3	O I	6.4
M II	221.9	N II	44.0	O II, III	3.3
M III	193.9	N III	37.3		
M IV	161.2	N IV	23.4		
M V	155.3	N V	22.3		
		N VI	4.5		
		N VII	4.3		

Emission lines: $M\alpha_1$ 151.0; $M\beta$ 156.7; $M\gamma$ 171.6; (M II N IV) 198.5; (M I N II, III) 204.7

Remarks	Intensity	rH	ν^*/R	Origin
Not accurate	1-2	139.7	126.4	F : $PtM\alpha_1 - 24.4 (N')$
—	2-3	149.6	144.9	F : $PtM\alpha_1 - 6.1 (N', O')$
—	2	152.6	150.7	F : $PtM\beta - 6.0 (N', O')$
—	1-2	155.4	156.3	M I : $CrK\alpha_1 - 242.5$
—	3	165.1	176.4	M II : $CrK\alpha_1 - 222.4$
—	5	177.7 _s	204.4	M III : $CrK\alpha_1 - 194.4$
—	6	191.4 _s	237.0	M IV : $CrK\alpha_1 - 161.8$
? Barely resolved	(?) 2	192.8	240.4	?
—	6	193.8 _s	243.0	M V : $CrK\alpha_1 - 155.8$
Difficult : inaccurate	1	207.0	276.9	M IV : $CrK\beta_1 - 161.1$
Difficult : inaccurate	1	209.2	282.9	M V : $CrK\beta_1 - 155.1$
—	1-2	231.7 _s	346.8	N I : $CrK\alpha_1 - 52.0$
—	2-3	234.7	355.6	N II : $CrK\alpha_1 - 43.2$
—	4	236.7	361.7	N III : $CrK\alpha_1 - 37.1$
Head of a narrow band	5	241.5	376.4	N IV, V : $CrK\alpha_1 - 22.4$
—	3	247.6	395.6	N VI, VII, O : $CrK\alpha_1 - 3.2$
Possibly inaccurate; recorded on one plate only	1	249.0	400.0	N III : $CrK\beta_1 - 38.0$
	1-2	254.0	416.3	N IV, V : $CrK\beta_1 - 21.7$
	0-1	259.0	432.7	N VI, VII, O : $CrK\beta_1 - 5.3$

In "The Photoelectrons expelled from Elements by Chromium K Radiations", by
H. R. Robinson, F.R.S., *Proc. Phys. Soc.*, 46, 696 (1934),
line 8, column 4, table 1

For 233.7 read 223.7.

Table 3. 74, tungsten (oxide)

Level-values, ν/R : M I	207.3	N I	43.3	O I	5.4
M II	189.3	N II	36.0	O II, III	2.9
M III	167.5	N III	31.0		
M IV	137.5	N IV	18.7		
M V	132.9	N V	17.6		
		N VI	2.3		
		N VII	2.0		

Emission lines: $M\alpha_1$ 130.8; $M\beta$ 135.1; $M\gamma$ 150.0; (M I N II, III) 176.5

Remarks	Intensity	rH	ν^*/R	Origin
—	2-3	131.2	111.5	F: $WM\alpha_1 - 19.3$ (N')
—	4	140.3	127.5	F: $WM\alpha_1 - 3.3$ (N', O)
Doubtful: inaccurate	2	142.8	132.0	F: $WM\beta - 3.1$ (N', O)
—	2	172.1	191.6	M I: $CrK\alpha_1 - 207.2$
—	3	180.1	209.8	M II: $CrK\alpha_1 - 189.0$
—	6	189.1	231.2	M III: $CrK\alpha_1 - 167.6$
—	6	201.1	261.4	M IV: $CrK\alpha_1 - 137.4$
—	6	202.9	266.1	M V: $CrK\alpha_1 - 132.7$
—	1-2	204.8	271.1	M III: $CrK\beta_1 - 166.9$
—	1-2	215.6	300.3	M IV: $CrK\beta_1 - 137.7$
—	1-2	217.5	305.6	M V: $CrK\beta_1 - 132.4$
—	2 -	234.7	355.6	N I: $CrK\alpha_1 - 43.2$
—	2 +	236.8	362.0	N II: $CrK\alpha_1 - 36.8$
—	3-4	239.1	369.0	N III: $CrK\alpha_1 - 29.8$
—	5	243.2	381.7	N IV, V: $CrK\alpha_1 - 17.1$
Head of a band	3	248.1	397.2	N VI, VII, O: $CrK\alpha_1 - 1.6$

Table 4. 62, samarium (oxide)

Level-values, ν/R : M I	127.2	N I	25.7	O I	3.0
M II	113.8	N II	20.0	O II, III	1.9
M III	104.9	N III	18.6		
M IV	81.8	N IV	10.0		
M V	79.8	N V	9.8		

Remarks	Intensity	rH	ν^*/R	Origin
—	3	205.2 ₅	272.3	M I: $CrK\alpha_1 - 126.5$
—	4	210.1	285.3	M II: $CrK\alpha_1 - 113.5$
—	6	213.5	294.5	M III: $CrK\alpha_1 - 104.3$
Not quite resolved	(?) 5-6	221.6	317.2	M IV: $CrK\alpha_1 - 81.6$
—	5-6	222.4	319.5	M V: $CrK\alpha_1 - 79.3$
Not clear: inaccurate	1-2	227.5	334.2	M III: $CrK\beta_1 - 103.8$
—	2	236.2	360.2	? Oxygen K: $CrK\alpha_1 - 38.6^\dagger$
Barely resolved	2	240.8	374.3	N I: $CrK\alpha_1 - 24.5$
Barely resolved	2	242.9 ₅	381.0	N II, III: $CrK\alpha_1 - 17.8$
Barely resolved	2	245.8 ₅	390.0	N IV, V: $CrK\alpha_1 - 8.8$
Barely resolved	1	248.5 ₅	398.6	N VI, VII, O: $CrK\alpha_1 - 0.2$

 \dagger Oxygen K level, $\nu/R = 39.3$ (Chalklin and Chalklin), or 38.8 (Thibaud). See reference (8).

Table 5. 57, lanthanum (oxide)

Level-values, ν/R :	L I 461.4	M I 101.0	N I 20.6	O I 3.0
	L II 434.7	M II 88.5	N II 15.0	O II, III 0.9
	L III 404.4	M III 82.5	N III 13.9	
		M IV 63.1	N IV 8.3	
		M V 61.8	N V 7.8	

Emission lines†: $L\alpha_1$ 342.6; $L\beta_1$ 371.4; $L\beta_2$ 396.6; $L\gamma_1$ 426.4

Remarks	Intensity	rH	ν^*/R	Origin
—	2	199.0	256.0	F: $LaL\alpha_1$ - 86.6 (M')
Narrow band: not clear	2	207.1	277.2	F: $LaL\alpha_1$ - 65.4 (M')
—	5	214.9 _s	298.5	M I: $CrK\alpha_1$ - 100.3
Not quite resolved	(?) 3	217.8	306.5	F: $LaL\beta_1$ - 64.9 (M')
—	4-5	219.2	310.4	M II: $CrK\alpha_1$ - 88.4
Not resolved	(?) 2	220.4	313.8	F: $LaL\beta_2$ - 82.8 (M')
—	6	221.2 _s	316.2	M III: $CrK\alpha_1$ - 82.6
Not resolved	(?) 5	227.1	333.1	F: $LaL\alpha_1$ - 9.5 (N')
—	5	228.6	337.5	M IV, V: $CrK\alpha_1$ - 61.3
Difficult: inaccurate	2	234.9	356.2	M III: $CrK\beta_1$ - 81.8. Probably also fluorescent lines
—	2-3	236.4 _s	360.9	F: $LaL\beta_1$ - 10.5 (N')
Not quite resolved	3	242.4 _s	379.4	N I: $CrK\alpha_1$ - 19.4
—	3	244.2 _s	385.0	N II, III: $CrK\alpha_1$ - 13.8
—	2	246.6	392.4	N IV, V: $CrK\alpha_1$ - 6.4
Inaccurate	0-1	248.7	399.1	O: $CrK\alpha_1$ - (-0.3)

† Some excitation of L II and L III sub-groups by $CrK\beta_1$ is to be expected, in addition to excitation by the harder components of the general primary radiation. $CrK\alpha_1$ just fails to excite the L levels of lanthanum.

In the first photographs taken with lanthanum, part of the copper backing of the chromium anticathode was exposed: as a result, the lines due to $CuK\alpha_1$ ($\nu/R = 592.7$) and shown in table 5a were recorded:

Table 5a.

Remarks	Intensity	rH	ν^*/R	Origin
Not accurate	2	142.2	130.9	L I: $CuK\alpha_1$ - 461.8
—	3	156.6	158.7	L II: $CuK\alpha_1$ - 434.0
—	6	170.8 _s	188.9	L III: $CuK\alpha_1$ - 403.8

Table 6. 50, tin (metal)

Level-values, ν/R :	L I 327.4	M I 63.9	N I 8.8	O I (-1.2)
	L II 304.9	M II 54.4	N II, III 5.3	
	L III 288.1	M III 51.2	N IV 0.6	
		M IV 35.1	N V 0.4	
		M V 34.4		

Emission lines: $L\alpha_1$ 253.7; $L\beta_1$ 269.8; $L\beta_2$ 287.7; $L\gamma_1$ 304.3

Remarks	Intensity	rH	ν^*/R	Origin
Inaccurate	1-2	103.5	69.4	L I: $CrK\alpha_1$ - 329.4
—	2-3	119.7	92.8	L II: $CrK\alpha_1$ - 306.0
—	5	129.9	109.3	L III: $CrK\alpha_1$ - 289.5
Not clear	1-2	151.6	148.8	L III: $CrK\beta_1$ - 289.2
Not sharp: head of a band	3-4	174.9	197.9	F: $SnL\alpha_1$ - 55.8 (M III')
Head of a band	6	182.3 _s	215.1	F: $SnL\alpha_1$ - 38.6 (M IV, V')
—	5	189.3	231.7	F: $SnL\beta_1$ - 38.1 (M IV, V')
Head of a band	3-4	197.3 _s	251.8	F: $SnL\beta_2$ - 35.9 (M IV, V'); $L\alpha_1$ - 1.9 (N', O')
Doubtful line	0-1	198.6	255.0	F: $SnL\beta_1$ - 14.8 (N')
Broad band	1-2	203.7	268.2	F: $SnL\beta_1$ - 1.6 (N', O')
—	5	227.6 _s	334.7	M I: $CrK\alpha_1$ - 64.1
Not fully resolved	(?) 5	230.8	344.0	M II: $CrK\alpha_1$ - 54.8
—	5-6	231.8 _s	347.1	M III: $CrK\alpha_1$ - 51.7
Double	4	237.4	363.8	M IV, V: $CrK\alpha_1$ - 35.0
Band: not sharp	1-2	247.0	393.7	N, O: $CrK\alpha_1$ - 5.1

Table 7. 47, silver (metal)

Level-values, ν/R : L I	282.0	M I	54.7	N I	8.7
L II	261.3	M II	46.1	N II, III	5.9
L III	248.6	M III	43.7	N IV	2.1
		M IV	29.2	N V	1.9
		M V	28.8		

Emission lines: $L\alpha_1$ 219.8; $L\beta_1$ 232.1; $L\beta_2$ 246.7; $L\gamma_1$ 259.2

Remarks	Intensity	νH	ν^*/R	Origin
—	2-3	135.3	118.6	L I : $CrK\alpha_1 - 280.2$
—	4	146.7	139.3	L II : $CrK\alpha_1 - 259.5$
—	6	153.3 ₅	152.2	L III : $CrK\alpha_1 - 246.6$
—	2-3	164.7 ₅	175.7	F : $AgL\alpha_1 - 44.1$ (M III'); AgL $\beta_1 - 56.4$ (M I')
Not resolved	(?) 2	169.6	186.1	F : $AgL\beta_1 - 46.0$ (M II')
Not resolved	(?) 3-4	170.7	188.5	F : $AgL\beta_1 - 43.6$ (M III')
Head of a complex band	6	171.5	190.3	F : $AgL\alpha_1 - 29.5$ (M IV, V')
Doubtful line	0-1	171.8 ₅	191.1	F : $AgL\alpha_1 - 28.7$ (M V')
—	4	177.2	203.1	F : $AgL\beta_1 - 29.0$ (M IV, V')
Head of a broad band	2	184.2	219.5	F : $AgL\beta_2 - 28.2$ (M IV, V'); L $\alpha_1 - 0.3$ (N')
—	1-2	186.1 ₅	224.1	F : $AgL\beta_1 - 8.0$ (N')
—	1-2	189.4	232.0	F : $AgL\beta_1 - 0.1$ (N', O')
—	4	231.7	346.7	M I : $CrK\alpha_1 - 52.1$
Not quite resolved	(?) 5	234.6	355.3	M II : $CrK\alpha_1 - 43.5$
—	5	235.3 ₅	357.6	M III : $CrK\alpha_1 - 41.2$
—	3-4	240.2 ₅	372.6	M IV, V : $CrK\alpha_1 - 26.2$
Head of a narrow band	2-3	247.8	396.2	N : $CrK\alpha_1 - 2.6$
—	1	252.9	412.6	M IV, V : $CrK\beta_1 - 25.4$

Table 8. 29, copper (metal)†

Level-values, ν/R : L I	81.0	M I	8.9
L II	70.3	M II, III	5.7
L III	68.9	M IV, V	0.4

Remarks	Intensity	νH	ν^*/R	Origin
—	6	222.0	318.3	L I : $CrK\alpha_1 - 80.5$
—	6 —	226.1	330.2	L II, III : $CrK\alpha_1 - 68.6$
Inaccurate: band with diffuse edge	2-3	246.2	391.2	M : $CrK\alpha_1 - 7.6$

† The experiments with copper were done under rather unfavourable conditions, and it was not possible to measure the M groups accurately.

§ 4. AGREEMENT WITH X-RAY DATA

It will be seen that with the values now adopted for the atomic constants there is in general good agreement between the photoelectric and crystal values of the X-ray terms, and that on the whole the agreement is best where the experimental conditions are most favourable. It will be obvious that when the photoelectric equation is used in this way to obtain term values, the experimental errors are greatest for the terms of lowest (negative) energy. For example, with a given element the M terms can be obtained much more accurately than the N.

Perhaps the most striking discrepancies are those in tables 6 and 7, for tin and silver. Although the consideration of the general question of numerical agreement is deferred to a later paper, it may be mentioned here that there is strong evidence that Siegbahn's values for the L and M levels of these two metals require fairly drastic revision^(9,10). It may therefore reasonably be assumed that part of the observed discrepancies is to be ascribed to inaccuracies in the X-ray data. It should however be pointed out at the same time that in some cases the photoelectric values are in better agreement with Siegbahn's summary tables than they are with recent direct determinations, for instance those of the gold and platinum M levels.

§ 5. RESOLVING POWER OF MAGNETIC SPECTROMETER

There are a number of points of general interest which emerge from the examination of these magnetic spectra. In the first place, the power and flexibility of the method are well illustrated by the way in which the M and N levels have been separated. All five M levels have been separated even for samarium (62). For lighter elements it is naturally not possible to separate M IV and M V, but M I, M II, M III, M V are separable for an element as light as silver (47). The spin doublets N IV, V and N VI, VII—the latter of which overlaps the O levels—are not resolved, but there is very fair separation of the other N levels right down to lanthanum (57).

This relatively high resolution is mainly due to the use of a fairly soft primary X radiation. Theoretically almost any degree of resolution is attainable by the use of sufficiently soft X rays, but unfortunately the more serious of the technical difficulties of these experiments increase rather rapidly with the wave-length of the primary X rays. Even with chromium K radiations the absorption is fairly high* and the photoelectrons are of such low energy that they are somewhat ineffective photographically. It seems probable that the work cannot be extended to much longer wave-lengths without some radical alterations in the apparatus and methods.

§ 6. RELATIVE INTENSITIES

The relative intensities of the lines are of special interest. The variation with the primary X-ray frequency of the relative intensities of the three lines in the L group and the five lines in the M group has already been discussed in some detail in references (1), (2), (4) and (5). The outstanding feature of the results is as follows: it is well known that when the frequency of the primary radiation is only a little higher than the highest critical absorption frequency of a group of levels, then the greater part of the absorption by that group is associated with the levels of larger k , according to the old $n_{k,l}$ notation for the levels. As the frequency of the X radiation increases, the levels of smaller k play a relatively greater part in the total absorption of the group, and finally at high frequencies their effect is predominant. The present work throws no new light on the general problem of absorption, but it very

* The intensity of a beam of chromium K α radiation is reduced to less than half value by absorption in a sheet of aluminium 0.02 mm. thick.

satisfactorily confirms and extends the information already obtained by this method at higher frequencies. The regularity with which these changes in relative intensity occur will be seen at once if the values listed above are compared with those shown in the diagram of reference (5), page 108.

§ 7. GENERAL

There are other points of interest in the appearance of the lines of the magnetic spectra. The line due to the conversion of the $\text{CrK}\beta_1$ line in a given level is always less clearly defined than that due to the conversion of $\text{CrK}\alpha_1$ in the same level. Comparison is rather difficult, as the former is always so much less intense than the latter, but the relative lack of sharpness of the lines due to $\text{K}\beta_1$ is noticeable on a great many of the plates. Such a difference is readily to be explained by the difference between the natural widths of the $\text{K}\alpha_1$ and $\text{K}\beta_1$ lines, but it is rather surprising that it should show up so prominently. It is also found that there are differences in sharpness between the lines corresponding to different levels, even when the lines are due to the same primary X radiation. It need hardly be said that these differences in the character of the lines are perceptible rather than measurable, and that they would be obscured by a very slight laxity in the control of the magnetic field during an exposure. They are however sufficiently marked to force themselves upon the attention of anyone habitually engaged in the measurement of the lines.

It is difficult to form a precise opinion upon the sharpness or otherwise of a set of lines, but the photographs as a whole leave an impression very much in accordance with the conclusion reached by Coster⁽¹¹⁾ as a result of his extensive and close study of X-ray emission spectra—namely that those levels are least sharply defined which have the greatest values for the ratio of their quantum numbers n/k . In terms of the old quasi-mechanical atom model, those levels are most diffuse which correspond to the orbits of greatest eccentricity. Thus, $\text{M}\nu$ is sharper than $\text{M}\iota$.

This question of the finite width of the X-ray lines and of the indefiniteness of the levels requires further attention, for it may appreciably affect the level-values measured by the photoelectric method when the accuracy is being pushed to the limit. The measurements are, with the semicircular focusing method, made on the high-velocity edges of the lines; what is measured is therefore something lying between the average and the maximum velocity of the electrons constituting the group, and depending to some extent upon the distribution of velocity and upon the peculiarities of the photographic plate. The resulting error is probably not large—the effect of the finite width of the chromium $\text{K}\alpha_1$ line is not likely to be more than about $0.1 \nu/R$ —but it is well to bear in mind that the photoelectric method, as used here, tends to give something approximating to a lower limit for an X-ray level.

§ 8. ACKNOWLEDGMENTS

In the course of this work it was necessary to take over eighty photographs of magnetic spectra, many of them being exposures of several hours' duration. I have pleasure in acknowledging my indebtedness to the Department of Scientific

and Industrial Research for a grant which enabled me to employ a full-time assistant and so to complete the work. I am also indebted to my assistant, Mr H. A. Nancarrow, M.Sc., for his share in the work; to the Research Department of the Metropolitan-Vickers Electrical Co. Ltd. for kindness in supplying me with chromium-plated copper sheets for use as anticathodes; and to Prof. E. H. Lamb for supplies of liquid air.

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A 5-KILOWATT X-RAY GENERATOR WITH A SPINNING TARGET

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ABSTRACT. A considerable increase in power can be obtained by moving the target of an X-ray generator. A detailed account is given of the design and construction of a successful machine in which the target is a water-cooled rotating disc.

§ 1. INTRODUCTION

THIS paper forms a sequel to three papers by A. Muller* in which he examines mathematically the power input limit of an X-ray generator, in the first paper for a circular focus on a stationary target, in the second for a circular focus on a moving target, and in the third for a line focus on both a stationary and a moving target.

A very great increase in the limit of power input is obtained by making the target in the form of a rotating disc. This has been done previously in sealed-off tubes, and large inputs have been obtained for a very short time after which the target has to be allowed to cool, mainly by radiation. If a large input is required continuously the target must be water-cooled; this means that the shaft must be brought out through a stuffing-box and that the vacuum must be maintained by continuous pumping.

For the machine described here Muller's formula gives 40 kw. as the limit of input power; this is with a line focus 1 cm. long and 1 mm. wide, the copper of the target being allowed to reach its melting-point. Cracking and roughening of the target, resulting in a decrease in X-ray intensity, occur well below the melting-point, and if the temperature-rise is limited to 300° C. the power-input limit is then 14 kw. If allowance is made for accidental local concentration of the cathode stream, due to hot spots on the filament or to imperfect focusing, the limit is considerably reduced still further. The machine works normally at 5 kw. and, at this power, has run for about 1000 hours of routine work during the past two years in addition to giving a very satisfactory performance during the experimental period.

The detailed description given is intended to show how a successful machine has been constructed. It is hoped that anyone interested and having some experience of design to suit the resources of a small workshop will find this description helpful in building a similar machine.

* *Proc. R.S. A*, 117, 30 (1927); 125, 507 (1929); 132, 646 (1931).

§ 2. OUTLINE OF DESIGN

The mechanical problem is to rotate a water-cooled copper disc in a vacuum while a stream of cathode rays is directed on to it from a suitably arranged cathode, the X-rays generated being allowed to emerge from a window with as little absorption as possible.

The disc is hollow and is mounted on the end of a hollow shaft which runs in ball bearings, passes out through a stuffing-box, and is driven by a belt and pulley while water circulates through the shaft and the inside of the disc.

The enclosure in which the disc runs is exhausted by a fast diffusion pump to a pressure at which the emission from a tungsten filament can be used as the source of cathode rays. The cathode is insulated and connected to a source of current at high tension.

The whole is mounted conveniently and rigidly on the wall of the room and provision is made for standing spectrometers in front of the window. Safety devices are provided to safeguard both the apparatus and the operator from accident or foolishness.

§ 3. THE MOUNTING OF THE TARGET DISC

Figure 1 shows a cross-section of the body of the machine with the target disc in place in its ball bearings. The body is in two parts, both of brass, one, 26, of which carries the ball bearings and vacuum stuffing, while the other, 2, forms the enclosure in which the disc rotates. The disc is built up of two parts, 3 machined from a solid piece of copper, and the back plate 6 of brass which is fitted and hard-soldered into 3; this has a boss 31 fitting into the part 30 which is clamped to the inner race of the ball bearing 9 by means of the nut 10. The outer race of this ball bearing fits a recess in 26 and is held in by the ring 8 and three small screws. A small grub screw 7 passing through 30, engages a slot in the boss 31 and prevents relative rotation of 31 in 30 while permitting the disc and its shaft to be withdrawn and replaced by another of steel or of copper coated with another metal whose characteristic radiation is required. The second ball bearing 21 at the other end is mounted in a similar way on the part 25 to which it is clamped by the ring 22; 25 is secured to the shaft by means of the grub screw 20, a hole being provided in 26 through which a screw-driver can be passed for this purpose. The outer race of this ball bearing is held in a recess in 24 by the ring 23, both 23 and 24 being fixed to 26 by three screws.

The hollow steel shaft 27 is hard-soldered into the boss 31 on the back plate 6; a smaller tube 28 is mounted concentrically in the baffle plate 4 which is carried on a perforated ring 5 from the inner surface of the back plate 6. The other end of 28 passes through a bush in the end of 27 to which it is soft-soldered. The water cooling the disc enters through the fitting shown in figure 3, passes up the smaller tube 28, and over the baffle plate, impinges on the inner surface of the copper 3.

and passes thence down the annular space between 27 and 28 and to waste through three holes near the end of 27.

The stuffing which renders the two glands in figure 3 water-tight is asbestos-graphite steam-gland packing.

The hard-soldering of the parts of the disc is somewhat difficult, for it must be absolutely water-tight and if water-tightness is not attained after one or two attempts the copper itself becomes spongy and leaks. A good test for water-tightness is to fill the disc with water and to run it at high speed while a polished surface is held to catch and detect any minute drops thrown off. If this test is passed, the joint is good.

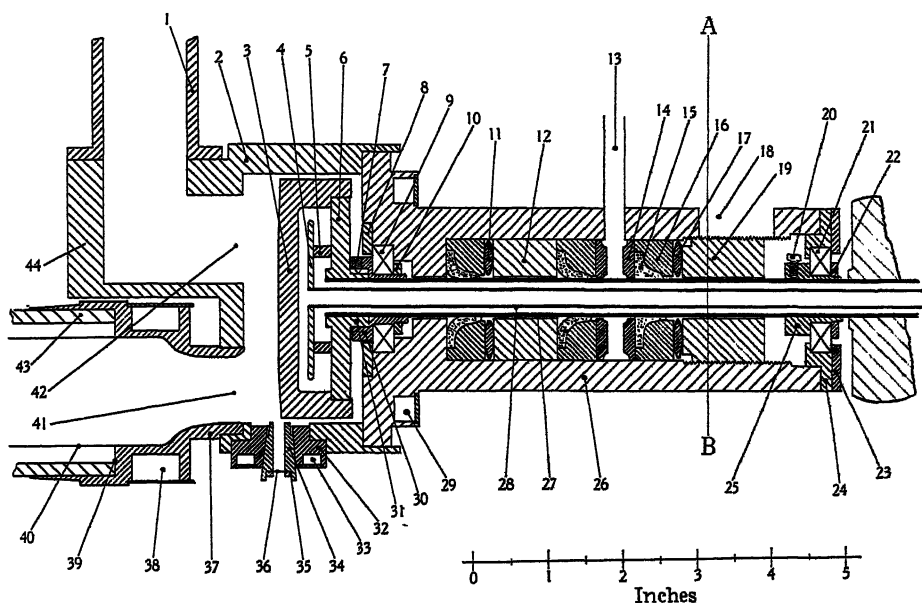


Figure 1.

§ 4. THE CASE AND WINDOW

The case 2 with the cubical boss 44 to which is attached the connexion 1 for the pump is machined out of a solid piece of brass.

Holes 41 and 42 are bored to take the support for the cathode 37 and to form the passage leading to the pump. A recess in 2 fits a flange on 26; the two parts are held together by six screws and the joint is made vacuum-tight with soft wax or, better, with apiezon plasticene. An end view is shown in figure 2, in which the parts are numbered to correspond with figure 1.

The part 37 which carries the glass tube supporting the cathode is made of steel and is fitted and soft-soldered into the hole 41 in 2. The glass tube 43 fits loosely in the open end and rests on the shoulder 39; a steel tube 40 protrudes some two or three inches and serves to remove electrical stress from the glass in

the neighbourhood of the joint. A plug 32 is soft-soldered into a recess in the side of 2 and into this fits the conical plug 34 which carries the thin aluminium window 36. This rests in a recess in 34 and is held in place with a ring 35 and a small quantity of sealing-wax, care being taken that no wax, which would seriously absorb X-rays, is allowed on either face of the window. The axis of the plug 34 lies in the plane of the disc which is slightly bevelled so as to allow X-rays from the whole length of the focus to pass through the window. The focus is formed along a radius of the disc and its foreshortened appearance as seen from the window is approximately circular.

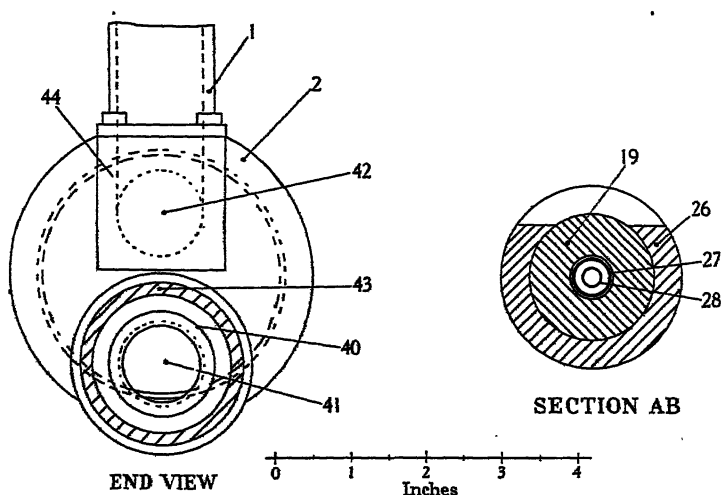


Figure 2.

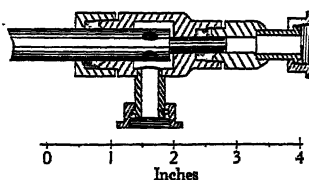


Figure 3.

The aluminium is punched with a cork-borer from a selected portion, free from pin-holes, of foil 0.001 in. thick. This absorbs about 19 per cent of copper radiation. Considerably less is absorbed by a window of beryllium, a small piece of which was distilled on to carbon in a cathode-ray furnace and subsequently ground to a suitable thickness. For some purposes, when a long collimating-tube is in use, this tube can be attached to the machine and a window of thin cellophane can be mounted on its end; in this way the absorption of the air is eliminated and the absorption of the window decreased. Secondary cathode rays must not be allowed to fall on the cellophane; if they do so a small magnet can often be arranged to deflect them.

Water cooling of the joint between 2 and 26, and of the window, is provided by channels 29 and 33 closed by rings fitted and soldered in recesses. Cooling of 37 is by water circulating in the channel 38 which is closed by a brass tube. Small nozzles made with slight swellings at their ends to hold rubber tubing firmly are fitted at convenient places. These should be hard-soldered in place so that they do not break off when the rubber tubing is pulled off.

§ 5. THE VACUUM STUFFING

The stuffing which fills the greater part of the body 26 is of special design. A hat-leather 15 fitting the shaft is compressed on to the shaft by means of a specially moulded rubber ring 16 which fits inside 26. Three stages are employed with an exhaust 13 communicating with the perforated ring 14 between the outer two.

All three stages are compressed together by the screw 19 which is turned by means of a tommy bar inserted into holes through the opening 18 cut in the side of 26. The force is communicated from the outer to the inner stages by the ring 14 and the distance piece 12.

The rings 17 and 11 are of lenticular cross section so that their area of contact with the rubber rings increases as the screw is tightened. The rubber is distorted and pressed against the inside of 26 and against the inner edges of the hat-leathers; in this way a compression which is readily adjustable is obtained, for the volume elasticity of rubber is very large, and if no space were left for distortion the pressure would rise very rapidly and adjustment would be more difficult. It is well to run the machine with the stuffing as loose as is consistent with a good vacuum. The hat-leathers are exhausted under molten vaseline in which they are allowed to cool; further vaseline is applied to the shaft as the stuffing is assembled. The rubber rings were made in a steel mould of appropriate shape to fit the hat-leathers.

In an earlier machine, which was quite successful, ordinary hemp in two stuffing boxes was used; the space between the boxes was exhausted and oil was allowed to suck through the outer stuffing from a reservoir into a detachable bulb from which it had to be transferred back to the reservoir from time to time. This return could be effected by means of a pump and a very satisfactory seal might be made in this way.

§ 6. THE CATHODE

A line focus is used so as to distribute the heat further; it is obtained from a hot filament with a shield having a slot in it. The support for the filament is shown in figure 4; it is made of steel and is seen in parts at the top of the figure and assembled at the bottom.

The rod 50 screws into 52 at one end and into 61 at the other. A screwed extension of 52 passes through the washer 53 and into the end of the conical part 55; this cone fits the conical hole in 54. When the rod and 61 are screwed up tight, the parts are held rigidly together and at the same time 54 is held firmly in the end of the main supporting tube 51. Mica insulation is wrapped round 55 and a mica

washer is inserted between 52 and 53. A projection 56 on the other end of 55 carries one clamp for the filament, and the arrangement of this clamp is shown in detail and enlarged in figure 5. A small plug fits a hole in 56 and has in it a small hole which fits the filament, a portion of this plug being filed away to permit the entry of the flat end of a screw which grips the filament securely. The other clamp for the filament is carried on the projection 58 on the end of 57; 57 and 58 are machined out of a solid piece which screws on to the front of 54.

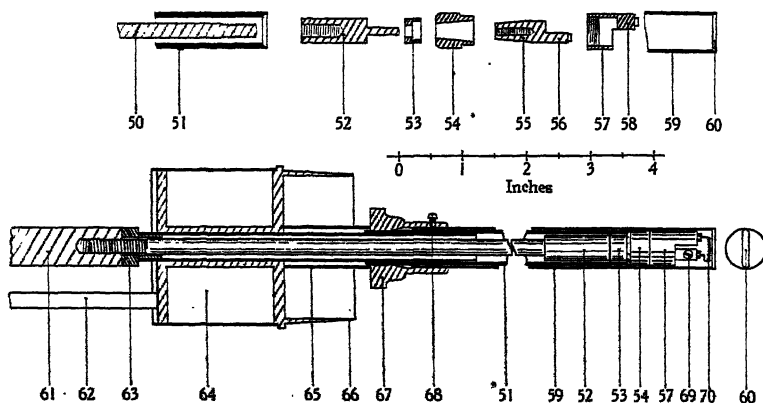


Figure 4.

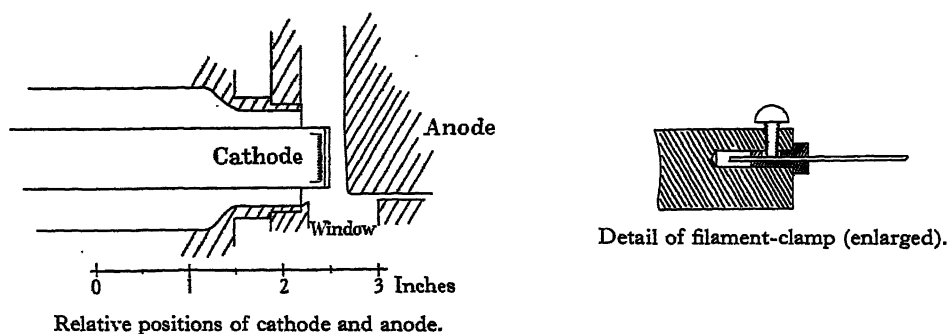


Figure 5.

This piece has, of course, to be screwed on while 55 is but loosely inserted in 54; the clamping portions 56 and 58 are then adjusted to be parallel and the rod 50 is tightened up by means of the nut 61.

Focusing is obtained by means of a slotted plate 60 made of the same metal as the disc in use and carried on the outer tube 59 which slides over 51 and is secured in position, with the slot 2 mm. in front of the filament, by means of the screw 68 passing through the fitting 67. The other end of this part 67 screws on to the split end of 51 and causes it to grip the smaller tube soldered into the end piece 64. This enables the distance from the slot to the surface of the target to be adjusted

to 4 mm. When this adjustment has been made, a distance piece 65 of the correct length is inserted to prevent slipping as the nut 61 is tightened. A bush of red fibre between 61 and the end of the tube completes the insulation of one of the electrodes; the electrical circuit is then completed through clamps on the end of 61 and the water pipes 62 which lead water into a channel surrounding 64. A tubular extension 66 fits loosely over the end of the glass tube which supports the cathode.

§ 7. THE FILAMENT

The filament is of tungsten wire 0.3 mm. in diameter, 22 turns of which are wound on a mandrel 1 mm. in diameter. This requires a heating current of 8.2 A. at 14 V. for an emission of 150 mA. The winding-machine is a piece of 1 mm. steel wire soldered in the tip of a 2 B.A. screw running in a nut that can be clamped in a block of brass; the tungsten is fed through a small hole in an extension from the block, and as a handle soldered to the head of the screw is turned the wire winds on the steel wire which is fed forward at the pitch of the screw. In this way a uniform spacing is obtained which avoids local over-heating. The ends of the tungsten are then bent at right angles and inserted into the clamps.

The filament should be mounted so that it is parallel to the slot, centrally placed, and 2 mm. behind the front edge of the slot; this distance is important, if it is too small the focus will not be sharp and there is risk of fusing the edges of the slot. The emission of 150 mA. will be obtained with a heating-current less than normal. If the distance is too large the heating-current has to be raised above normal to obtain the emission, and the filament will rapidly evaporate and cover the target with a deposit of tungsten.

The distance from the slot to the target should be 4 mm.; if this distance is too small, sparking will occur and it will not be possible to raise the voltage to the normal running value of 30 kV. If it is too large, the machine will generate high-frequency oscillations and behave very much as if it were leaking. After inserting a new filament and pumping to a good vacuum— 10^{-4} mm. of mercury—the filament should be run at normal current for 10 minutes with the disc rotating but without the high tension.

§ 8. ASSEMBLY AND MOUNTING

The generator is shown assembled in figure 6. The cathode is supported on two glass tubes, the joints being made with short lengths 80, 82, 84 of electro-deposited rubber cycle tube; if these are washed with alcohol as they are put on they form a very good vacuum joint. Such joints have been used successfully in similar apparatus since 1929. The tube 81, supported on the flange 83 between the two glass tubes, is intended to reduce the potential-gradient; it may not, however, really be necessary for this purpose, but it is useful for centering the cathode by sliding the glass tubes on the flange.

The generator is clamped in a large plummer block bolted to a girder which is fixed to the wall. The girder also carries an adjustable table and a Leybold four-

stage mercury diffusion pump. A closed steel tube made by boring a solid bar is mounted inside the main pipe from the pump; solid carbon dioxide is packed into this and mercury vapour is thereby prevented from getting into the machine.

A Pirani gauge mounted on the top of 2 (fig. 6) is used as an indicator of leaks; this was supplied by courtesy of the Research Laboratories of the General Electric Company. The disc is driven at 2000 r.p.m. by a pulley 86 and belt from a 1-h.p. motor which is separately mounted on the wall. Next to the pulley is a centrifugal switch 87 which is connected by two slip-rings and brushes in circuit with the operating coil of the main contactor, so that if the disc should stop for any reason the power is switched off.

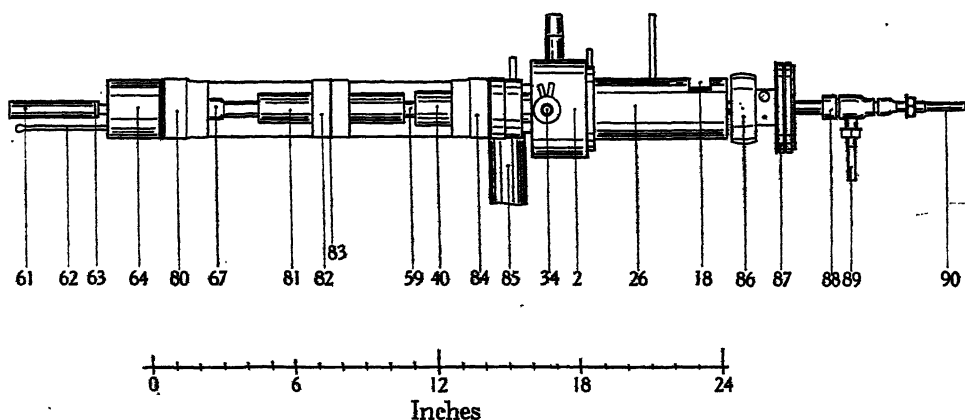


Figure 6.

88, 89, 90 are the water connexions for cooling the disc already described (p. 704 and fig. 3). From the outlet pipe a small branch pipe leads up to one of the mercury switches on the wall. These switches are operated by the pressure of the water as it emerges from a slightly constricted outlet in each water circuit and they switch off the power if the water fails. A small contactor and ammeter are in circuit with the electric heater of the diffusion pump; and the operating coil of this contactor is in circuit with a mercury switch operated by the cooling-water of the pump.

A large conical-ended shield completely encloses the cathode and its supporting tubes. The water and electrical connexions are led to the end of the cathode through a brass tube supported along the axis of the shield from a large paxolin column 4 ft. long and 5 in. in diameter; on this are wound two 30-ft. lengths of $\frac{1}{4}$ -in. rubber tube to provide insulation for the water cooling the cathode. This rubber must be kept dry and should be protected from the effects of ozone with a coat of varnish applied after it has been wound on the paxolin. Shellac can be used but it is liable to crack, and then the rubber is attacked by ozone and very soon breaks down. A more flexible varnish can be obtained from insulator-manufacturers and is very much better for the purpose.

§ 9. ELECTRICAL CIRCUIT

The current of 150 mA. at 30 kV. supplied to the generator is obtained from a 5-kw., centre-tapped transformer specially made by Schall and Son, Ltd., and two rectifying valves giving biphasc rectification. The valves must be capable of withstanding a back voltage double the working peak value and of passing a current of 150 mA. continuously; valves having the necessary characteristics can be obtained commercially.

The body of the generator is connected to earth and the current returns to the centre tapping of the transformer through a milliammeter. A high resistance of 10 M Ω . in series with a milliammeter reading up to 5 mA. is connected from the

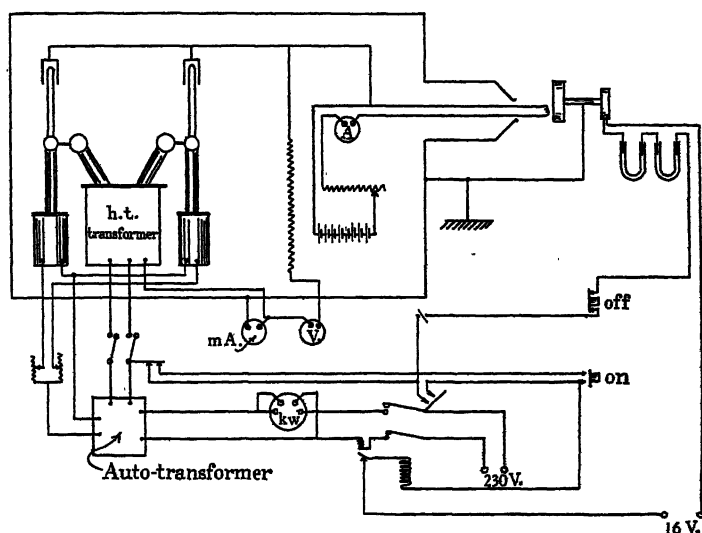


Figure 7.

high-tension terminal of the generator to the centre tapping and indicates the voltage. The input is controlled by means of variable tappings on an autotransformer and a variable series resistance.

A contactor operating on 16 V. by a push button connects the 230-V. supply to an autotransformer, and this at once heats the valve filaments through two transformers with insulated low-tension secondary windings. A manually operated switch is then used to turn on the high-tension transformer: a back contact on this switch wired in series with the "on" button ensures that the valve filaments shall be hot before the h.t. can be turned on. A series of safety contacts in the operating circuit of the contactor renders the electrical apparatus as fool-proof as possible. The centrifugal switch and the water-operated mercury switches have been mentioned; in addition there is a contact on the door of the enclosure protecting the transformers and valves.

§ 10. ACKNOWLEDGMENTS

The machine described was designed and constructed in collaboration with Dr Alex Muller, the assistant director of the Davy Faraday Laboratory, where the work has, for the greater part, been carried out. Thanks are due to Mr H. Smith who has collaborated throughout in the construction and testing of the machine and is now responsible for running and maintenance; to the workshop of the Royal Institution and in particular to the head of this workshop, Mr C. H. Jenkinson, for making the machine and for many suggestions connected with the mechanical design; to Mr Mitcham, for help in setting up the electrical equipment; and to the Research Laboratories of the General Electric Company for their continued friendly interest and hospitality for several months during the rebuilding of the Royal Institution. Finally, the author acknowledges his indebtedness to the director and managers of the Royal Institution for their interest in the work.

THE ESTIMATION OF SMALL DIFFERENCES IN X-RAY WAVE-LENGTHS BY THE POWDER METHOD

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ABSTRACT. It has been found possible by the use of a microphotometer to determine accurately the positions of lines at high angles of reflection on a powder photograph. With a powder photograph of clear colourless quartz taken with copper K_{α} radiation, the distance apart of the two component lines of a well-resolved doublet was measured to within 0·0002 cm. The measurements were then corrected for systematic errors—eccentricity of specimen, absorption of the radiation in the specimen, and divergence of the X-ray beam. The wave-length difference ($\lambda_2 - \lambda_1$) was finally calculated in terms of the given wave-length λ_1 . The value of ($\lambda_2 - \lambda_1$) for copper K_{α} radiation is given as 3·833 X.

§ 1. INTRODUCTION

DURING a study of the use of quartz for the calibration of X-ray powder cameras* it was found that the K_{α} doublets at high angles of reflection had very sharp peaks. The most highly resolved doublets are so far apart that their peaks are not likely to be displaced as a result of overlapping of their bases. This can be seen from figure 1*a*, which is a photometric record† for the doublet for which $h, k, l = 2, 3, 4$, readings being taken at intervals of 0·01 cm. From a detailed survey of the summits of these lines, with readings at intervals of 0·001 cm., figure 1*b*, it appears* that the position of the peaks can be measured to $\pm 0\cdot0001$ cm.

From such measurements it should be possible to make accurate estimates of small differences of wave-length. An interesting problem is the measurement of the difference between the copper K_{α_2} and K_{α_1} wave-lengths in terms of the given copper K_{α_1} wave-length.

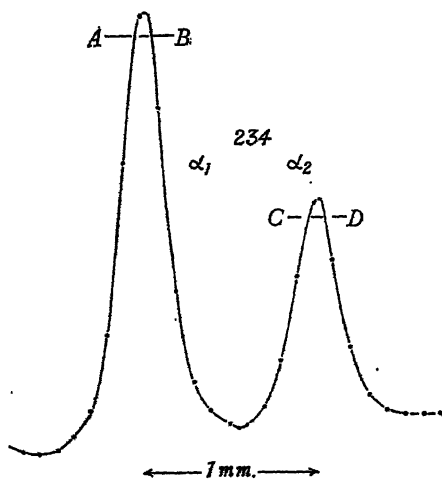
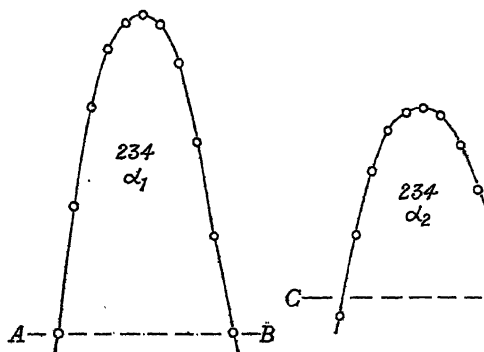
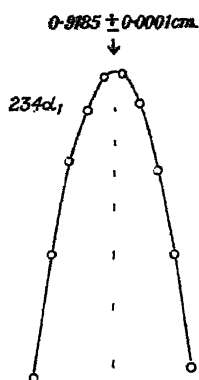
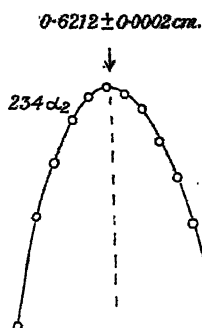
§ 2. EXPERIMENTAL MEASUREMENTS

Special precautions were taken to find the positions of the peaks. Figures 1*b*, 2*a* and 2*b* show typical curves obtained from photometer readings taken at intervals of 0·001 cm. near the summits of the 2, 3, 4 doublet on both sides of the film. The exact position of maximum density cannot be read off the curve directly because the top is rounded. In order to find the true position of a peak, measurements corresponding to midway between points of equal blackening on either slope of the record curve were found. If the curve is symmetrical the most probable value is given by the bisectors at different heights, as in table 1. Where the summits are slightly

* A. J. Bradley and A. H. Jay, *Proc. Phys. Soc.* 45, 507 (1933).

† Obtained with a microphotometer made by the Cambridge Instrument Co., Ltd.

asymmetrical, figure 2*b*, the bisectors show a drift, table 2. Here the position of the peak is given as the value the bisector would have at the top of the curve. The examples mentioned above were the extreme cases of symmetry and asymmetry.

Figure 1*a*.Figure 1*b*. Readings at intervals of 0.001 cm.Figure 2*a*.Figure 2*b*.

Readings at intervals of 0.001 cm.

Table 1

Line 2, 3, 4 α_1		Side 1	First adjustment
Position of points of equal blackening on either side of line. (cm.)			Bisector. (cm.)
0.9144	0.9226		$\frac{1}{2}(1.8370)$
0.9150	0.9220		$\frac{1}{2}(1.8370)$
0.9158	0.9211		$\frac{1}{2}(1.8369)$
0.9170	0.9201		$\frac{1}{2}(1.8371)$
		Peak: $\frac{1}{2}(1.8370) = 0.9185 \pm 0.0001$ cm.	

Table 2

Line 2, 3, 4 α_2	Side 1	Second adjustment
Position of points of equal blackening on either side of line (cm.)		Bisector. (cm.)
0.6171	0.6258	$\frac{1}{2}$ (1.2429)
0.6176	0.6251	$\frac{1}{2}$ (1.2427)
0.6184	0.6241	$\frac{1}{2}$ (1.2425)
0.6195	0.6229	$\frac{1}{2}$ (1.2424)
		Peak: $\frac{1}{2}$ (1.2424) = 0.6212 \pm 0.0002 cm.

The film was reset in the photometer and a second series of measurements was made. The results for the 2, 3, 4 $\alpha_1\alpha_2$ doublet, for both sides of the film, are given in table 3.

Table 3

Side 1			Side 2		
Position of peaks (cm.) 2, 3, 4 α_2	2, 3, 4 α_1	Separation (cm.)	Position of peaks (cm.) 2, 3, 4 α_2	2, 3, 4 α_1	Separation (cm.)
First adjustment					
0.8186	0.9185	0.0999	0.3702	0.4700	0.0998
\pm 0.0001	\pm 0.0001	\pm 0.0002	\pm 0.0002	\pm 0.0001	\pm 0.0003
Sum of separations on both sides of film: 0.1997 cm.					
Second adjustment					
0.6212	0.7210	0.0998	0.6751	0.7748	0.0997
\pm 0.0002	\pm 0.0001	\pm 0.0003	\pm 0.0002	\pm 0.0001	\pm 0.0003
Sum of separations on both sides of film: 0.1995 cm.					
Average for two series of measurements: 0.1996 cm.					

The measurements in table 3 give the difference $S_2 - S_1$ between the S values for the 2, 3, 4 α_2 and 2, 3, 4 α_1 lines, S being the distance between corresponding lines on either side of the film. Before calculating the difference between the wave-lengths, it is necessary to correct the measurements $S_2 - S_1$ for a number of systematic errors. These arise from (i) the eccentricity of the specimen; (ii) the absorption of the radiation in the specimen; and (iii) the divergence of the X-ray beam.

§ 3. CORRECTIONS FOR ECCENTRICITY OF SPECIMEN, ABSORPTION AND DIVERGENCE OF THE X-RAY BEAM

The glancing angle θ is related to the measurement S by the relation $S = 4R\theta$, R being the radius of the camera. It has, however, been shown that owing to film-shrinkage R cannot be considered to be a constant. It is most convenient to use for deriving θ from S a formula which allows for film-shrinkage. This formula* is $S/S_k = \theta/\theta_k$ where S_k is the length of film corresponding to a known angle θ_k , which

* A. J. Bradley and A. H. Jay, *Proc. Phys. Soc.* **44**, 563 (1932).

is a constant for the camera. The value of S_k depends in the same way as S on the film shrinkage.

The following measurements* were obtained by means of a travelling microscope:

$$S_k = 26.443 \text{ cm. where } \theta_k = 82.77^\circ.$$

$$S_1 = 24.517 \text{ cm.}$$

The angle θ_1 corresponding to S_1 is given by the relation

$$\begin{aligned}\theta_1 &= \theta_k \cdot \frac{S_1}{S_k} \\ &= 76.741^\circ.\end{aligned}$$

The value of θ for the 2, 3, 4 α_1 reflection can also be calculated from Bergqvist's† value of the d_{100} spacing of quartz, and the axial ratio $c/a = 1.10002^*$. The calculated

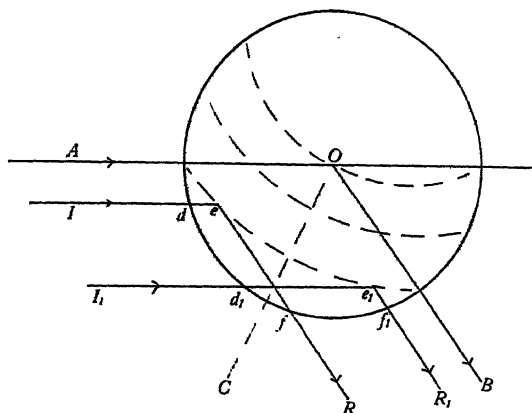


Figure 3.

value of θ after correction for refractivity is 76.790° . The difference 0.049° between the observed and calculated values is due to the systematic errors, and may be used as a measure of the corrections which must be applied to the doublet separation.

The systematic errors arise chiefly from the eccentricity of the specimen, but a small additional effect, introduced by absorption, may be calculated from its known radius.

A simple examination, following the method of Claassen‡, shows the effect of absorption on the line-position. Reference is made to figure 3. A powdered specimen of uniform density§ is bathed in a parallel beam of X-rays. AO is the direction of the incident beam and OB the direction of the reflected beam. Consider the incident beam I and the reflected beam R . The beam I enters the specimen at d , travels a distance de before reflection and a distance ef after reflection, and leaves the

* A. J. Bradley and A. H. Jay, *Proc. Phys. Soc.* 45, 507 (1933).

† O. Bergqvist, *Z. f. Phys.* 66, 494 (1930).

‡ A. Claassen, *Phil. Mag.* 9, 57 (1930).

§ Continual rotation of the specimen simulates this condition.

Estimation of small differences in X-ray wave-lengths by powder method 717

specimen at f . The distance travelled through the specimen is $(de + ef)$. From any point of scattering e , the intensity of the reflected beam will be given by

$$I = kI_0 e^{-\mu(de + ef)}.$$

Similarly for the ray $I_1 d_1 e_1 + e_1 f_1 R_1$

$$I = kI_0 e^{-\mu(d_1 e_1 + e_1 f_1)}.$$

Other factors being equal, the intensities of the reflected beams are equal when $(de + ef) = (d_1 e_1 + e_1 f_1)$.

Scattering points which contribute equal effects lie on a curved surface, such that the sum of the distances travelled through the specimen before and after reflection is a constant. There are an infinite number of these surfaces, each having its own path-difference. The curves are symmetrical about a direction OC , where $A\hat{O}C = C\hat{O}B$.

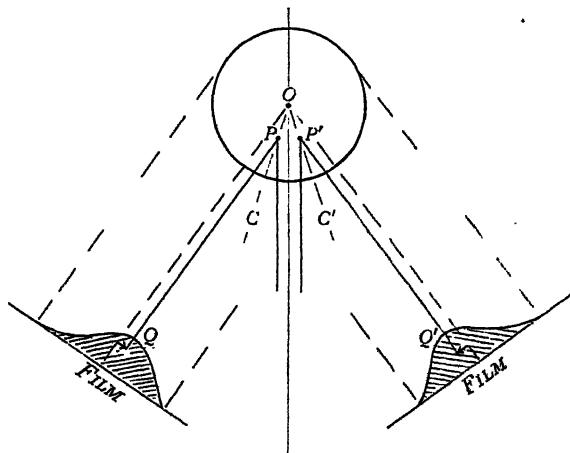


Figure 4.

Consider a line on the film, the peak of which has been displaced to a higher angle owing to absorption of the radiation in the specimen, see figure 4. The peak may be regarded as coming from the point P , the centre of the scattering source. P will be displaced from the centre of the specimen in the direction OC . Similarly, for the corresponding reflection on the other side of the film the centre of scattering may be regarded as being at some point P' .

It is difficult to make an accurate estimate of the shift OP , which must depend on the size of the specimen, absorption of the radiation in the specimen, and the position of the line on the film.

The use of a thin diluted specimen of transparent material, such as quartz, with copper K_α radiation, reduces this shift to a small amount, and the high-angle reflections will tend to be symmetrical in shape. In fact photometer measurements show that the quartz line $h, k, l = 2, 3, 4$ is symmetrical to a high degree. The displacement OP must therefore be small.

Since the two scattering centres P and P^1 are not on the axis of the system, an error is introduced by the divergence of the X-ray beam from the point X , figure 5. The ray PQ for a parallel beam is swung round to PS , making QPS equal to ϕ . The angle ϕ is given by $\sin \phi = OP \cdot \sin \hat{POX} / PX$. Consider a specimen, 0.3 to 0.4 mm. in diameter, giving a reflection at $\theta = 75^\circ$. Suppose that $PX = 10$ cm. and assume that OP is one quarter of the radius of specimen, then $\phi = 0.006^\circ$. The measured angle of deviation is then too large by a ϕ , and so the measured glancing angle is too large by an amount 0.003° . The angle would therefore be 76.738° for a parallel beam.

A small correction in the separation of the doublet is also necessary because of the displacement of the two scattering centres P and P^1 , one for either side of the film, from the centre O of the specimen. The displacement OP or OP^1 may be resolved into two components, (i) a displacement OO^1 along the axis of the system,

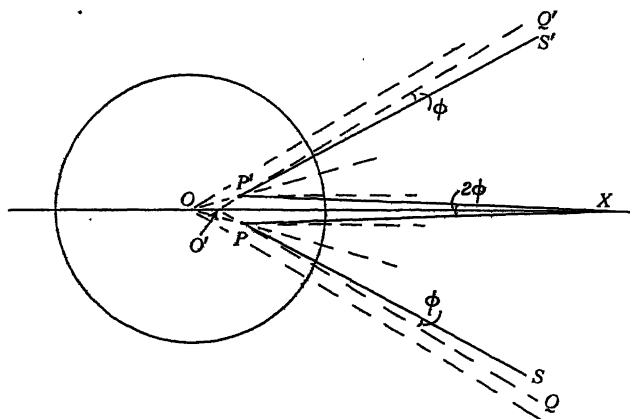


Figure 5.

which simply introduces a numerical modification in the eccentricity factor, and (ii) a displacement O^1P or O^1P^1 . The second effect is considered separately. Its effect is to increase the doublet separation in the ratio $(R + O^1P) : R$. The correction to be applied in the present instance is 0.0001 cm., giving a doublet separation of 0.1997 cm.

Eccentricity of scattering source. The shift of the lines on the film to smaller measured angles, for instance the shift of 2, 3, 4 α , from 76.790° to 76.738° , is due to the displacement of the scattering source away from the incident beam. In figure 6 a line is displaced a distance x in the direction of the arrow, owing to a shift in the position of the specimen. The distance x may be calculated from the error $(76.790^\circ - 76.738^\circ)$ in the measured angle for 2, 3, 4 α , and the radius 4.576 cm. of the film. Thus

$$x = R \cdot \sin 2(76.790^\circ - 76.738^\circ).$$

This shift is equivalent to an increase dR in the effective radius of the film at this point, where

$$x = dR \cdot \tan(\pi - 2\theta).$$

Estimation of small differences in X-ray wave-lengths by powder method 719

Combining the above equations, we find $dR = 0.017$ cm. The observed separation of the component lines of the doublet is proportional to the distance of that part of the film from the scattering source, and is therefore increased in the ratio dR/R . Hence the observed separation 0.1997 cm. is 0.0007 cm. too great, and the correct value is 0.1990 cm., equivalent to an angular separation ($\theta_2 - \theta_1$) of 0.6229° .

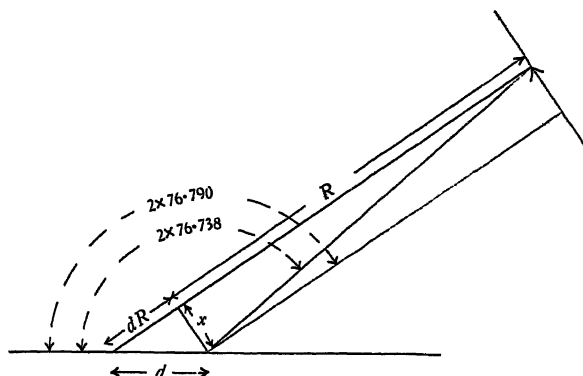


Figure 6.

§ 4. CALCULATION OF $\lambda_2 - \lambda_1$

From the Bragg relationship $2d \cdot \sin \theta = n\lambda$ we have the difference in wave-lengths given by the expression

$$\begin{aligned} \lambda_2 - \lambda_1 &= \lambda_1 \frac{\sin \theta_2 - \sin \theta_1}{\sin \theta_1} \\ &= \frac{2\lambda_1}{\sin \theta_1} \cdot \cos \left(\frac{\theta_2 + \theta_1}{2} \right) \cdot \sin \left(\frac{\theta_2 - \theta_1}{2} \right). \end{aligned}$$

The accuracy of $(\lambda_2 - \lambda_1)$ is governed almost entirely by the angular separation $(\theta_2 - \theta_1)$, which is equal to 0.6229° . By substitution in the above equation the value of $\lambda_2 - \lambda_1$ is given as 3.833 X. for copper $K_{\alpha_1 \alpha_2}$ radiation.

The data in table 4 for copper $K_{\alpha_1 \alpha_2}$ radiation are taken from the latest edition of Siegbahn's *Spektroskopie der Röntgenstrahlen**.

Table 4

Year	Wave-lengths (X.)		Difference (X.)	Author
	λ_2	λ_1		
1924	1541.19	1537.32	3.87	Lang
1925	1541.02	1537.29	3.73	Leide
1926	1541.15	1537.30	3.85	Schorr
1929	1541.243	1537.396	3.847	Siegbahn
1930	1541.232	1537.395	3.837	Wermerlof

The value now obtained, 3.833 X., is in very good agreement with the latest of the above values.

* Julius Springer, Berlin (1931).

§ 5. ACKNOWLEDGMENT

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A TIME-BASE CIRCUIT AND ELECTRON RELAY FOR USE WITH A CATHODE-RAY OSCILLOGRAPH*

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ABSTRACT. The ordinary sealed-off type of cathode ray oscillograph is adapted to form a relay capable of picking out accurately points on a current or voltage wave to be investigated by means of a second cathode-ray oscillograph. A time-base circuit and the amplifier for the relay are described also.

§ 1. PRINCIPLES OF THE METHOD

EARLIER work of the British Electrical and Allied Industries Research Association on the shape of the voltage-recovery wave at arc-extinction, was based on experiments made with a circuit of very small scale, an ordinary sealed-off cathode-ray oscillograph, and repeating phenomena. Methods employing an oscillograph capable of giving transient records of single voltage-rises had therefore to be developed. This note is concerned with the technical problems which have arisen in connexion with these experiments and it is hoped that their solution may have applications in other electrical and particularly in switch-gear problems.

On the Wood oscillograph employed the recording space is very limited, being that of a photographic plate $2\frac{1}{2}$ in. by $1\frac{1}{2}$ in. To get a record of recovery voltage lasting about 2×10^{-4} sec. the spot must traverse the plate in, say, 5×10^{-4} sec. This is, of course, a very moderate speed of recording for the present-day type of cathode-ray oscillograph. The difficulty that arises is that the spot cannot be allowed to oscillate backwards and forwards along the plate, waiting for the phenomenon to happen, as this would cause excessive fogging of the plate. From twenty to thirty traverses would be made for every half-cycle at standard frequency. A further drawback of this procedure is that the time scale would almost necessarily have to be sinusoidal, and therefore inconvenient for measurement; moreover it would render almost useless any record which happened to come at either end of the scale where the speed of traverse is small. On the other hand the type of phenomenon investigated by means of the high-voltage cathode-ray oscillograph invariably takes the form of a very rapidly rising voltage of high value. This allows of the use of the three-spark-balls method of tripping the time-scale mechanism. Generally a condenser is charged up to a high voltage and has in parallel with it the time deflection plates of the oscillograph, together with a resistance in series with the two outer of the three spark balls. The centre ball is connected in some way to the circuit

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in which the high-voltage wave to be investigated occurs. When the surge arrives the rapid change of potential of the centre ball upsets the equilibrium, so that a spark takes place across the two gaps in succession, the capacity is discharged and the time-scale sweep is thus operated. In the mean time the phenomenon passes along a delay cable so as to arrive at the other pair of deflection plates of the oscillograph just after the time-scale sweep has been started.

In the present investigation this scheme had to be ruled out for various causes. For instance, the voltage-changes are not necessarily characterized by a steep wave-front, and though there is such a front at arc-break the "arcing volts" previous to it must also be recorded. For this purpose a long delay cable would be necessary, and this would alter the nature of the voltage investigated.

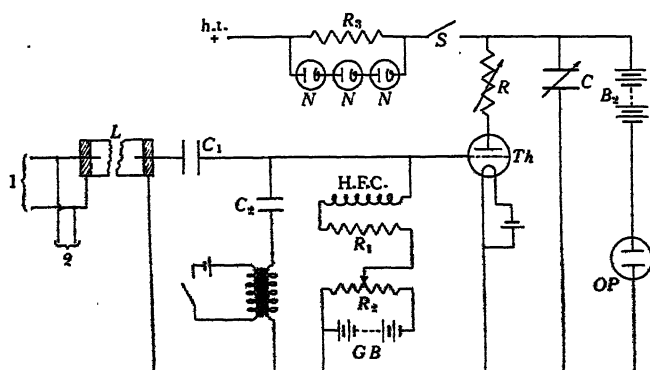


Figure 1. Thyatron time-scale circuit.

The time-scale circuit actually used is in principle the same as that described above. The spark balls are replaced by a thyatron relay, and the potential-change on its grid which causes it to trip at the required moment is not initiated by the voltage surge but by a special cathode-ray relay tube operating in conjunction with the current in the switch circuit which is a locked quantity inasmuch as the voltage surges and oscillations to be investigated occur just before and after a current zero.

Figure 1 shows the time-scale circuit in detail. The condenser C is charged up to about twice the potential required to deflect the spot completely across the recording plate of the oscillograph. The deflecting plates are at OP and a bias battery B_2 is used to adjust the initial position of the spot, which is just off the recording plate. The potential on C is maintained through the resistance R_3 , which is several megohms, the switch S being closed. By means of the potentiometer R_2 and grid-bias battery GB the grid of the thyatron Th is kept at a potential with respect to its filament which is 5 or 10 volts more negative than the tripping potential. The tripping impulse, which must be positive, is supplied by an amplifier at terminals 1 and passes along a shielded low-capacity line L to a condenser C_1 of $0.01 \mu F$. and then on to the grid. A high-frequency choke H.F.C. and a grid-bias resistance R_1 are inserted between the grid and the potentiometer R_2 to prevent the impulse from passing back to earth.

On the arrival of the impulse on the grid the thyatron flashes, and the charge from the condenser C flows through the non-inductive resistance R . The potential across C therefore falls off exponentially, exactly the same fall occurring across the deflection plates OP . Normally the thyatron would be extinguished after this discharge since the current from the h.-t. batteries or rectifier through R_s cannot be made large enough to keep the thyatron burning without affecting the exponential discharge of C adversely. R_s is, however, so large that the recharging of condenser C takes place more rapidly than the closing of the shutter of the camera, with the result that bad over-exposure and fogging of the plate occur. To avoid this several neon lamps N are placed in parallel with R_s . When the potential on C has fallen to a value at which the spot has been swept completely off the plate, the neon lamps flash, passing enough current to keep the thyatron alight but not enough to cause an appreciable drop of potential across R . The strength of the current is adjusted to the desired value by the use of considerable resistance in series with the neon lamps themselves. In this way the spot does not return after the thyatron has been tripped. After the camera shutter has been closed, switch S is opened and closed and the time-scale is ready for the next test.

§ 2. THE TRIPPING-MECHANISM

The first method of tripping tried out was based on a suggestion made by Mr A. P. Paton of the Electrical Research Association. The beam of light from an electromagnetic oscillograph recording the current in the main circuit was allowed to fall on a photoelectric cell as the vibrating mirror passed through its zero position. To make the timing sufficiently accurate, the velocity of the beam at the cell had to be large and a very narrow stop in the form of a slit had to be placed in front of the cell. This caused the light-flux to be so small that the electric impulse given by the cell was too small to be amplified successfully.

The principle of the method as now used for tripping the time scale will be understood by reference to figure 2. The heavy lines represent the main circuit containing the switch S under investigation. CT is a current transformer which supplies current to two coils C_1 and C_2 placed on either side of a special relay tube. This is essentially a permanent vacuum cathode-ray oscillograph, but instead of having a large conical end with a fluorescent screen the tube is cylindrical, somewhat longer than usual and has an electrode E at its end. When alternating current flows in the main circuit and therefore in the coils C_1 and C_2 the spot, which in the undeflected position falls on E , is deflected perpendicularly to the plane of the paper passing across E each time the current passes through a current zero. This causes a charge to fall on E at each current zero. E is connected to the grid of the first valve of an amplifier A and the output of the amplifier is used to trip the thyatron and initiate the time-scale movement as explained above. To prevent this from happening before the occurrence of the current-zero at which the record is to be taken, the output of the amplifier is temporarily short-circuited. As the switch S opens, its moving contact opens a selector switch SS after it has travelled a selected

distance. *SS* then operates a low-capacity switch by means of a thyatron relay *SR*, opening the short-circuit on the amplifier. The voltage across the switch at the next current-zero is therefore recorded. With a gas-blast switch, as developed by the Electrical Research Association, there is no difficulty whatever in predetermining the current-zero at which the arc will be extinguished, so that records of the recovery voltage at the final current zero can be obtained. With the ordinary plain break in oil, however, nothing of the kind can be done. This method of recording then becomes a hit-or-miss method. For plain break in oil, therefore, a special resetting time scale which will not fog the photographic plate during resetting will have to be constructed*, and several voltage records must be made on the same photographic plate at each test.

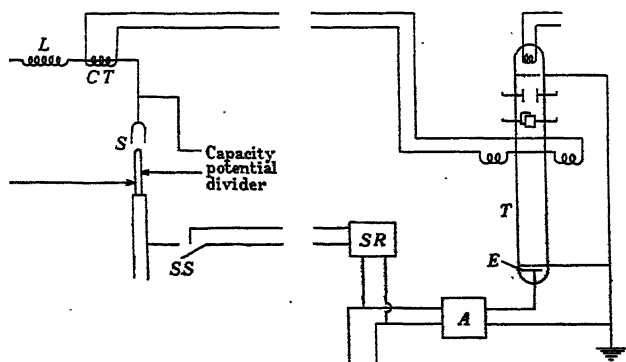


Figure 2. General scheme of tripping circuit.

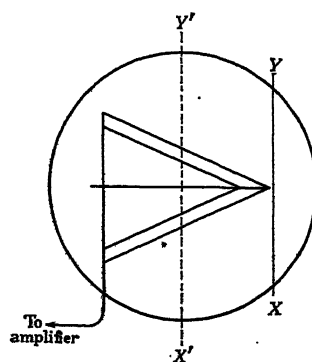


Figure 3.

The electrode *E* and the amplifier *A* are of special construction. Figure 3 represents the end of the tube on which in normal running the phenomenon is recorded, i.e., the fluorescent screen. The electron stream is, of course, perpendicular to the plane of the paper and represented by a spot on figure 3. The deflection coils *C*₁ and *C*₂, figure 2, are arranged on the oscillograph so that when current flows in them the spot is deflected along the line *XY*, figure 3. With a sinusoidal current flowing in the coils the spot therefore moves up and down *XY* in simple harmonic motion. With a frequency of 50 c./sec. the velocity of the spot as it passes through its zero position (corresponding to the zero of current) is $314A$ cm./sec., where *A* is the amplitude of the swing in centimetres. *A* can be altered at will by changing the number of ampere-turns in the coils. The time taken by the spot to move 1 mm. is thus $0.1/314A$ sec., so that the amplitude required to make it move 1 mm. in 10 microseconds is 32 cm. approximately. There is no difficulty in producing such an amplitude. Even if the tolerance in the tripping-time were 1μ sec., requiring an amplitude of 320 cm., the apparatus would function perfectly provided harmonics in the current wave were not too great. Corrections could be made by altering the phase of the current in the coils. When the correction, as is generally

* This has now been done, 7/8/1934.

the case, would mean an advancement of the current in the coils, a very simple arrangement is used to effect it.

On reference again to figure 3 it will be seen that the electrode has a special shape. *AB* and *AC* are two strips of metal foil, *AO* and *BC* metal wires. *AO* is perpendicular to the line *XY* along which the deflections of the spot take place. The spot is set somewhere along *AO*, say at *M*, which is then its zero position. It moves along *X'Y'* when current flows in the coils. As the spot approaches from the upper half of the half-cycle, it meets the electrode at *b* before it has come to its zero position *M*. The impulse which trips the time-scale therefore occurs $L/3142A$ sec. before the actual current-zero, where *L* is the distance *Mb* in millimetres. The same time-advancement is obtained when the current approaches zero from the opposite direction. To vary *L* all that need be done is to shift the zero position of the spot along *AO*, a very simple operation. Hence the time scale can be tripped at any preselected time before current-zero*.

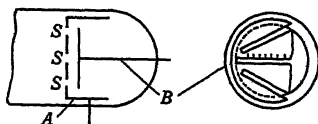


Figure 4.

This type of electrode, however, had a serious defect. In a sealed-off tube, where a certain amount of gas focusing is relied upon, positive-ion space charges surround the electron stream itself. The tube also depends for its successful operation on secondary emission from the fluorescent screen forming the return path to the anode. Hence these additional electrodes, being practically at earth potential which is the potential of the anode, act as collectors for all such charges formed in the neighbourhood. The result is that no sudden change of potential takes place when the electron stream proper falls on such an electrode. The potential rises gradually as the beam approaches it and this rise in potential is much too slow to be of any use in the accurate timing required. The electrode system was therefore modified as shown in figure 4.

A similar method of producing a time-advancement is incorporated, but three slots in an earthed shield *A* now take the place of the electrode in figure 3. The earthed shield collects practically all the stray current and all the current from the beam except when the electrons fall on one of the slits, when they pass through to the electrode *B*, which is connected to the amplifier. A scale for positioning the spot is provided along one edge of the centre slot. The divisions are 5 mm. apart†.

The electrode of the cathode-ray relay tube cannot be connected directly to the grid of the thyatron, as the impulse is in the wrong direction. A single-valve amplifier may be interposed but much better results can be obtained by using a three-valve amplifier‡ of special design.

* See Appendix 2.

† These tubes were made by Mr L. H. Bedford of A. C. Cossor and Son.

‡ Appendix 3.

Alternating current of 50 c./sec. is passed through the deflecting-coils of the cathode-ray relay tube and also through a similar pair of deflecting-coils on another cathode-ray oscillograph of the sealed-off type. In the relay tube the spot is thus caused to move simply-harmonically along a line perpendicular to the centre slot in the earthed shield. The electric impulses falling on the shielded electrode as the beam sweeps across are amplified and applied to one of the deflecting plates of the oscillograph so as to produce deflections perpendicular to that produced by its

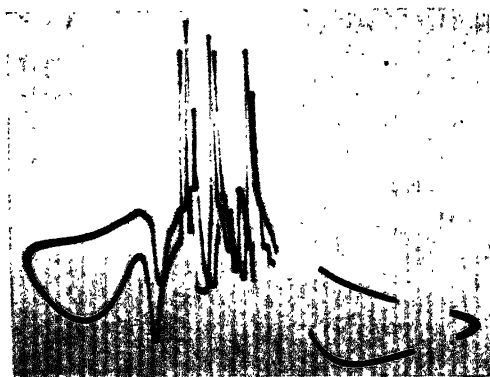


Figure 5.

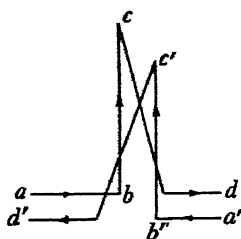


Figure 6.

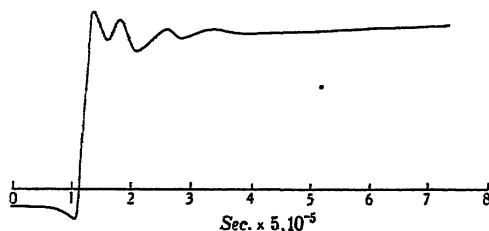


Figure 7. Trace of cathode ray oscillogram of voltage across h.-t. switch at current-zero, the time-scale device of oscillograph being tripped by the electron relay tube.

current coils. In this way a stationary picture showing the impulses as the spot traverses the slots in the relay is obtained. In figure 5 six prominent peaks are seen corresponding to the six edges of the three slots*. Those shown correspond to potentials of about 50 V. from the zero line.

The accuracy with which the thyatron can be tripped depends on the steepness with which the voltage rises to one of these peak values. This can be determined by comparing the two peaks corresponding to any one of the three slots. In figure 6, *ab*

* What appears to be a seventh prominent peak as well as other raggedness in the picture is due to a complicated mixture of interference and under-damping of the amplifier. This has no effect on the operation of the apparatus.

represents the beam approaching the left-hand edge of a slit, bc represents the impulsive rise when the beam crosses the edge and cd the dying away of the impulse. When the beam approaches the slit from the opposite direction the sequence of events will be represented by $a'b'c'd'$, where bb' will be the width of the slit. Now if the rises were instantaneous bc and $b'c'$ would be parallel, but if they were slow cc' would be less than bb' . Hence by measuring these quantities the time taken by the voltage to rise from b to c can be deduced.

Figure 7 is an oscillogram taken by this method. The timing-wave has a frequency of 2×10^4 .

§ 3. ACKNOWLEDGMENTS

The author is greatly indebted to Mr L. H. Bedford of A. C. Cossor and Son, who was responsible for the making of the relay tube. Thanks are also due to Mr L. Gosland, of the Electrical Research Association, whose help was invaluable in solving the many problems of electric and magnetic interference which arose.

APPENDIX 1

DISCHARGE OF CONDENSER THROUGH THYRATRON

The thyatron constitutes a back e.m.f. of about 16 V. during the discharge of the condenser. If q is the charge on the condenser at any instant and ϵ the back e.m.f. of the thyatron then

$$R \frac{dq}{dt} + \epsilon + \frac{q}{C} = 0,$$

$$q + \epsilon C = A e^{-t/RC},$$

$$e = E e^{-t/RC} - \epsilon (1 - e^{-t/RC}),$$

where e is the e.m.f. across the condenser at any instant and E the e.m.f. of the h.-t. battery. Since E is about 700 V. and $\epsilon \doteq 16$ V. the effect of the thyatron becomes important only near the end of the time scale.

APPENDIX 2

ADVANCEMENT PRODUCED BY THE PHASE-ADVANCER

We assume firstly that the main circuit current is sinusoidal, that no third harmonic is present, and that the current transformer functions perfectly. As the anode potential can be varied usefully in making the settings, the sensitivity may conveniently be defined by the equation

$$\sqrt{500} S_{cm} / V_e^{\frac{1}{2}}$$

where S_{cm} is the deflection in centimetres for 1 ampere-turn at an anode potential of 500 V., and V_e is the anode potential applied to the relay tube.

If i is the r.m.s. current in the deflecting coils and n the number of turns, then the amplitude A of swing of the spot will be given in centimetres by

$$A = \sqrt{2} \cdot ni \sqrt{500} \cdot S_{cm} / V_c^{\frac{1}{2}}.$$

The velocity v of the spot near its zero position is therefore given by

$$v = 314 \sqrt{2} \cdot \sqrt{500} \cdot ni S_{cm} / V_c^{\frac{1}{2}}.$$

If d is the distance of the outer edge of the slot from the centre line the advancement-time T will be given in seconds by

$$T = V_c^{\frac{1}{2}} d / 314 \sqrt{1000} \cdot ni S_{cm}.$$

Using in place of d the more convenient quantity x shown in figure 8, and writing

$$d = Kx,$$

we have

$$T = Kx V_c^{\frac{1}{2}} / 314 \sqrt{1000} \cdot ni S_{cm}.$$

This time T is the time required to bring the indication at current-zero to a convenient position on the photographic plate. The time-scale sweep starts at A , figure 9, just off the recording-plate, and ends at B , which is well off the plate, so that the sweep over the plate is roughly linear.

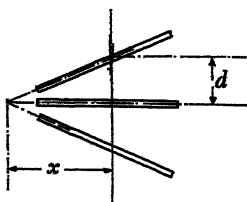


Figure 8.

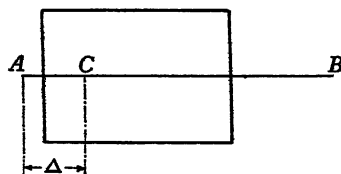


Figure 9.

As the anode-potential of the main oscillograph may be varied also, its electrostatic sensitivity can be conveniently expressed in cm. per volt by the equation

$$5 \times 10^3 S_s / V,$$

where S_s is the deflection in centimetres for 1 V. on the deflecting-plates when the anode voltage is 5,000.

Hence if l is the total length of the sweep and E the e.m.f. of the h.-t. battery used in producing the sweep*, the distance Δ through which the spot has moved from A in time T will be given by

$$\Delta = l - l e^{-T/RC} + \frac{lE}{E} (1 - e^{-T/RC}).$$

To a first approximation, when T/RC is small compared with unity, the effect of the thyatron being left out of account,

$$\begin{aligned} \Delta &= lT/RC \\ &= \frac{5 \cdot 10^3 S_s}{V} E \frac{T}{RC}. \end{aligned}$$

* See Appendix 1.

This assumes that there is no time lag between the instant at which the spot strikes the edge of the slot and the tripping of the thyatron; but the lag will become appreciable in very fast time scales and it will then be necessary to write $T - \tau$ for T in the above equation, thus

$$T = \tau + \Delta RCV / 5 \cdot 10^3 S_s E.$$

Hence
$$\frac{Kx V_0^{\frac{1}{2}}}{314 \sqrt{1000 \cdot ni S_{cm}}} = \tau + \frac{\Delta RCV}{5 \cdot 10^3 S_s E}.$$

All these quantities can be measured experimentally except τ . A group of values of x , n , i and Δ or x and Δ only, all other quantities being kept fixed, will enable a graph to be plotted giving the value of τ . In the experiments made with our equipment the presence of the third harmonic in i and of imperfection of the current transformer caused systematic errors greater than τ . These, however, can be allowed for by graphing groups of results in the same manner as for τ .

For experimental work where i varies from test to test it has been found convenient to write

$$x = \zeta RCVni / V_0^{\frac{1}{2}}$$

where ζ varies with the current in the main circuit. The deflecting coils are easily changed for others having a different number of turns, or may be connected in series or parallel. ni is chosen so as to make $\zeta RCVni / V_0^{\frac{1}{2}}$ as nearly equal to the mean value of x as possible, and the final adjustment is made with x .

APPENDIX 3

THE VALVE AMPLIFIER

The design of the amplifier, shown diagrammatically in figure 10, is very important from the point of view of reproducing the very steep peaks as accurately as possible. In fact the amplifier can be made to sharpen them up and it is on this

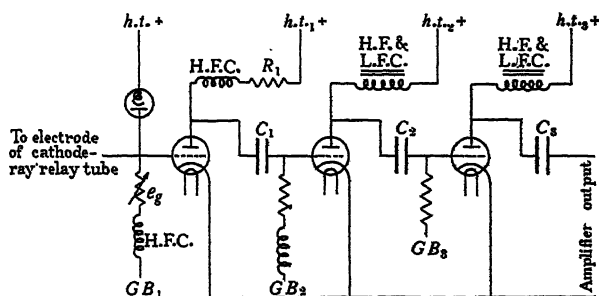


Figure 10.

account only that the relay tube works as successfully as it does. Two points must receive special attention in design in order to produce the desired results. Firstly, a steady potential applied to the grid of the first valve must not be reproduced as a steady potential across the output, while any changing potential on the first grid must be reproduced as a potential-maximum or minimum. The second point is that the potential on the first grid may mount up to values dangerous for the valve, as the

electrode of the relay tube can rise or fall to the anode-potential of the tube, generally 500 to 800 V. As the d.-c. amplification is not quite negligible, this growth of grid-potential may have other results besides endangering the valve. Hence a grid leak of small resistance, or the neon-lamp device described later, must be used.

The grid leak consists of a variable low-capacity resistance of about 10,000 Ω . A low-resistance variable high-frequency choke would do even better service here. One electrode of a decapped neon-lamp is also connected to the grid, the other electrode being connected to about 140 V. h.-t. positive. Hence if the grid becomes more than 30 V. or so negative with respect to the filament of the valve, the neon strikes, thereby protecting the grid from further increase of negative voltage. This only happens when the beam of the cathode-ray tripping-tube is kept directly on the shielded electrode. Generally the low resistance of the grid leak is sufficient protection; its effect is to allow the grid to return rapidly to equilibrium potential after receiving an impulse, such impulses being all of the same sign.

The anode circuit of the first stage consists of a resistance and high-frequency choke with capacity coupling to the grid of the next valve. The anode circuits of succeeding stages are choke-capacity-coupled. This gives the desired emphasis to de/dt rather than to e .

When the potential of the grid becomes suddenly more positive the anode current increases. At first this increase in current will cause a fall of potential on the grid of the next valve, the impedance of the choke to changes of current being high. When steady conditions return, the potential at the anode returns to the battery-potential if the d.-c. resistance of the choke is negligible, and so the potential on the second grid returns to its original value also, even though the potential on the first grid remains changed.

Values of circuit constants. In ordinary valve-circuit notation the increase in plate current i_p due to a change of grid-potential e_g and of plate-potential e_p is given by

$$i_p = G_{cp} e_g + G_p e_p,$$

where G_{cp} is the mutual conductance and G_p the plate conductance of the valve. i_p is made up of two parts, one from the plate-circuit choke and one from the grid capacity of the next valve; hence

$$i_p = i_c + i_x;$$

$$e_x = -L \frac{di_c}{dt};$$

and

$$i_x = -C \frac{de_p}{dt},$$

where C is the grid capacity of the next valve.

From these equations we have

$$\frac{di_p}{dt} = \frac{di_c}{dt} + \frac{di_x}{dt}.$$

$$\therefore G_{cp} \frac{de_g}{dt} + G_p \frac{de_p}{dt} = -\frac{e_p}{L} - C \frac{d^2 e_p}{dt^2}.$$

$$\therefore C \frac{d^2 e_p}{dt^2} + G_p \frac{de_p}{dt} + \frac{e_p}{L} = -G_{cp} \frac{de_g}{dt},$$

or, in operational notation,

$$(D - m_1)(D - m_2)e_p = -\frac{G_{cp}}{C}De_g,$$

where

$$m_1, m_2 = -\frac{1}{2C} \left\{ G_p \pm \sqrt{G_p^2 - \frac{4C}{L}} \right\}.$$

The best case will clearly be when e_g is a unit function of the time. Then

$$\begin{aligned} e_p &= -\frac{G_{cp}e_g}{C(m_1 - m_2)} \left[\frac{D}{D - m_1} - \frac{D}{D - m_2} \right] 1 \\ &= -\frac{G_{cp}e_g}{C(m_1 - m_2)} [\epsilon^{m_1 t} - \epsilon^{m_2 t}]. \end{aligned}$$

Write

$$m_1 = -\alpha + \beta \quad m_2 = -\alpha - \beta$$

so that

$$\alpha = G_p/2C, \quad \beta = \sqrt{G_p^2/4C^2 - 1/LC},$$

$$\therefore e_p = -\frac{G_{cp}e_g}{C \sqrt{G_p^2/C^2 - 4/LC}} e^{-\alpha t} (e^{\beta t} - e^{-\beta t}) \quad \dots\dots(1).$$

There are two ways in which this expression for e_p may be made to approximate initially to a unit function, i.e. in which $(de_p/dt)_0$ may be made as large as possible. Physically these two methods are (1) by making L very large and C very small, and having valves of as high mutual conductance G_{cp} as possible. It is clear that any increase in the plate current will cause charge to flow from the condenser C rather than through the inductance L , thus rapidly altering the potential on the next grid. G_p must be chosen so that the circuit is not oscillatory. (2) By making the circuit highly oscillatory, i.e. with a very high natural frequency, L and C being both small. Changes in i_p amount to the application of impulses to this circuit, causing it to oscillate at this high frequency. This arrangement too will give a high rate of change of $(de_p/dt)_0$. There is a possibility, however, that the amplitude of this oscillation may be so small as to give less satisfactory results than the previously described arrangement. The former arrangement is indeed the better; this can be shown as follows. From equation (1) it is clear that the condition to be satisfied is that β must be real and numerically less than α , and further the difference between α and β must be as small as possible, i.e. $4/L$ must be small in comparison with G_p^2/C . Hence G_p and L must be large and C small. Since this is to be the case we may write

$$\begin{aligned} \beta &= (\alpha^2 - K^2)^{\frac{1}{2}} = \alpha (1 - K^2/\alpha^2)^{\frac{1}{2}}, \quad K = 1/\sqrt{LC} \\ &= \alpha (1 - K^2/2\alpha^2) = \alpha - \delta \end{aligned}$$

where

$$\delta = K^2/2\alpha^2 = 1/2LC\alpha^2.$$

Then

$$\alpha + \beta \approx 2\alpha \text{ and } \alpha - \beta = \delta,$$

and equation (1) can be written

$$e_p = -\frac{G_{cp}e_g}{C \sqrt{G_p^2/C^2 - 4/LC}} (\epsilon^{-\delta t} - \epsilon^{-2\alpha t}) \quad \dots\dots(2).$$

For a rapid rise in e_p , therefore, α must be as large as possible. If most of the rise is to occur in time t_0 then $2\alpha t_0 = 1$, and if $t_0 = 10^{-6}$ sec. then $2\alpha = G_p/C = 10^6$. If $G_p = 10^{-4}$ mho., C would have to be 10^{-10} F., which is possible, C being the grid earth capacity of the valve.

The amplitude factor in equation (2) contains G_p in the denominator and it therefore decreases as G_p is increased, so that G_p must be made small and G_p/C large. Hence the principal practical requirement in the construction of the amplifier is to have C as small as possible, and then to choose G_p so as to make G_p equal to $10^6 C$. Next $4/L$ must be very much less than G_p^2/C ; for instance, $L = 400 C/G_p^2$, while $C = 10^{-11}$ F., $G_p = 10^{-5}$ mho.; and L would have to be 40 henries. These are all practicable values.

The oscillatory arrangement will be considered briefly. In equation (1) write

$$\beta = \frac{1}{2C} \sqrt{\left(\frac{4C}{L} - G_p^2\right)}.$$

Then

$$\begin{aligned} e_p &= -\frac{G_{cp} e_g}{j\beta} e^{-\alpha t} [e^{j\beta t} - e^{-j\beta t}] \\ &= -G_{cp} e_g \sqrt{LC} \cdot e^{-\alpha t} \sin \beta t. \end{aligned}$$

The oscillation frequency must be of the order of 10^6 c./sec., i.e. β must be of the order of $5 \cdot 10^6$. Since β comes in the denominator of the amplitude term, the latter will be extremely small, about 10^{-11} of the value of the same term in the other arrangement.

DISCUSSION

Prof. G. I. FINCH said that the author's device might be usefully adapted to the control of switch-gear for the purpose of opening a circuit at the instant when the current is passing through its zero value.

Mr R. S. WHIPPLE said that the method would save a good deal of expense by reducing the amount of film that normally had to be expended to ensure that a particular phenomenon of brief duration was recorded.

REVIEWS OF BOOKS

Introduction to Theoretical Physics, by J. C. SLATER and N. H. FRANK. Pp. xx + 576. (New York and London: McGraw-Hill Publishing Co., Ltd., 1933.) 30s. net.

This is an excellent book, particularly well designed to supplement existing English texts, from which it differs radically in treatment. It might well, as the authors point out in their preface, have been alternatively entitled "An introduction to the methods of theoretical physics," and it may be especially recommended to those students who already have an adequate knowledge of experimental physics and who wish to become more closely acquainted with the technique of the mathematical side of their subject.

More than half of the book is rightly devoted to a concise but reasonably consecutive account of the classical mechanics and theoretical physics. This is treated on modern lines, and leads naturally to the development and applications of wave and statistical mechanics to which chapters 28-42 of the book are devoted. Within the obvious limitations of space the treatment is remarkably comprehensive; and the value of the book to students is enhanced, and the text to some extent supplemented, by an extensive collection of exercises and problems.

Introduction to Modern Physics, by F. K. RICHTMYER. Pp. xviii + 747. (London and New York: McGraw-Hill Publishing Co., Ltd.) 30s. net.

The author of this, one of the most important of modern text-books, has earned the thanks of the present generation of learners and teachers, in that he has refused to alter seriously the scope of the book. As users of the work are well aware, the first three chapters, some eighty pages in all, are concerned with an admirable historical treatment which leads us from Thales to Maxwell. The rush of modern discovery must have sorely tempted the author to cut down his introduction in order to admit the work of yesterday, but he has wisely resisted the temptation, even at the price, for example, of the omission of any discussion of cosmic radiation. The work develops on orthodox lines. Following the historical introduction, we have chapters on electromagnetic theory, the photoelectric effect, the quantum theory and its application to specific heats, spectra and the nuclear atom, the vector model of the atom, X-rays, the nucleus, and a final chapter on wave-theory. In this edition the chapter on the photoelectric effect has been extended and that on the nucleus re-written. The chapters on the wave-theory and on the vector model of the atom are new.

It will be seen that the author has interpreted the term "modern" in no narrow sense, and his scholarly, and *thoroughly physical*, treatise is to be welcomed as a valuable addition to our pedagogical literature.

A. F.

L'Univers en Expansion, by Sir ARTHUR EDDINGTON, translated by J. ROSSIGNOL. Pp. xii + 166. (Paris: Hermann et Cie., 1934.) 15 francs.

This is the French translation of that very famous work, *The Expanding Universe*. Mainly intended for the intelligent layman, it has also a particular interest for the physicist. If any there be who, like the present reviewer, failed to be much impressed by the paper in which the masses of the electron and proton were calculated, they can read its arguments rather more cogently set out here.

The book deals with much more than the observational material which led to the concept of an expanding universe, this being dealt with in the first chapter. The next two chapters deal with the more theoretical reasons for expecting to find such a state of affairs, whilst the last chapter discusses, as has been implied above, the "argument of the 137" and the question "relatively to what is the universe expanding, and why do we not say instead that the contents are contracting?" The book is fascinating to read, its distinguished author displaying once again that lightness of touch, combined with sureness, for which he is well known.

The translation into French is on the whole happy, but the translator seems to have missed the point in his version of the lines which run in the original:

"He thought he saw electrons swift
 Their charge and mass combine;
 He looked again and saw it was
 The cosmic sounding line.
 The population then, said he,
 Must be 10^{79} ."

Perhaps we cannot expect him to be familiar with Lewis Carroll, but the facts that the second, fourth and sixth lines rhyme and particularly that the last one scans have been lost in the translation.

J. H. A.

The Thermodynamics of Electrical Phenomena in Metals, by P. W. BRIDGMAN.

Pp. vi + 200. (London: Macmillan and Co., Ltd.) 16s.

The volume under review is essentially the substance of a number of papers which Prof. Bridgman has written during the last ten years on inter-relations of a thermodynamic character between various electrical properties of metals. The substance of these papers has now been consolidated into a coherent whole and published in book form.

The author points out that the development of the great fundamental concepts of physics is often a slow process, and this is particularly true of the theories of the electrical properties of matter. The historical development of the fundamental ideas spread over a long time; sixty years from Poisson to the formulation of the field equations for stationary bodies by Maxwell, to pick out two important landmarks.

The experience underlying the equations of Maxwell was a fairly exhaustive knowledge of electrical phenomena in empty space. The electrical properties of matter are, however, most complicated and many of them have been discovered since the crystallization of the concepts. Among the various properties of matter with which this book is specially concerned are the following: thermo-electric properties, including Peltier and Thomson thermal effects; the Volta effect; thermionic emission; photo-electric emission; cold discharges in intense fields; phenomena in crystals, including anisotropic resistance and various reversible heating effects; and various effects in the magnetic field, of which the Hall effect is the best known.

Prof. Bridgman has set himself the task of scrutinizing each of these effects to find whether it fitted into the scheme of fundamental concepts or whether modification was demanded. In the course of his enquiry he finds that there are relations between the various effects which are demanded by the broad general principles of thermodynamics. Apart from the intrinsic interest of these relations, many of which are new, they are of importance in directing the development of any detailed theory because it is necessary that the theory be capable of giving an account of them.

Another important conclusion arrived at is that the concepts in terms of which the attempt has been made to describe the electrical state inside a metal are not broad enough, but have to be amplified in a way which turns out not to be difficult.

E. G.

Operational Methods in Mathematical Physics, by H. JEFFREYS. Pp. vi + 117. (Second edition, Cambridge University Press.) 6s. 6d. net.

The first edition of this tract is probably better known to physicists than any other of the Cambridge Mathematical Tracts, and the second will be as useful. We may regret the disappearance of the discussion of Heaviside's generalized experimental series, but the sentiment is quite irrational. For the benefit of those who are not acquainted with the work, it may be said that the operational methods dealt with are those developed by Heaviside rather than those due to Boole. Heaviside did not know the reason why his methods worked, and the omission was repaired by Bromwich, who used the theory of contour integration, and later by Carson, who used integral equations. The present tract follows the path opened up by Bromwich, and is probably the only work not devoted solely to electrical networks which gives a connected account of the subject. Readers should not miss the first page, where the author, a Cambridge mathematician be it remembered, quotes Heaviside's remark, "Even Cambridge mathematicians deserve justice," nor the last page, where some penetrating remarks on differential equations have replaced the peroration of the first edition. If, in passing from the first to the last page, they follow the direct and not the retrograde route, they will be wise.

J. H. A.

Cartesian Tensors, by H. JEFFREYS. Pp. vi + 92. (Cambridge University Press.) 5s. net.

Notation is a most important matter. Neither the D-ists nor those in their dot-age could have discovered Lagrange's equations in dynamics, because neither could express concisely the formula which we write $\frac{d}{dt} \frac{\partial T}{\partial \dot{q}_r} - \frac{\partial T}{\partial q_r} = Q_r$. Again, we all like to name the point (x, y, z) as P so as to avoid frequent repetition of the group of symbols, but it is an advance to replace x, y and z by x_1, x_2 and x_3 and to abbreviate the three to x . The summation convention of tensor analysis is an analogous device. Dr Jeffreys has had the very useful idea of introducing the student to the tensor notion and notation in the particular case where the axes are always rectangular. Transformations are thus always linear and some of the difficulties of the general theory are consequently avoided, though its advantages are retained.

The applications of the theory to mechanics, including elasticity and hydrodynamics, are given, and the book is provided with that necessity for the true student, examples to be worked by the reader. It should do much to contribute to a wider knowledge of the subject, and is an excellent introduction to the more advanced treatises.

J. H. A.

The Scientific Journal of the Royal College of Science, volume 4. Pp. 172. (London: Edward Arnold and Co.) 7s. 6d.

This journal has reached its fourth annual volume and the editing committee is to be heartily congratulated on its success. To attempt to fulfil the double function of giving to the specialist a convenient and scholarly résumé of his own subject, and of assisting the layman in these matters to some comprehension of the work of the specialist, is to court disaster. But it can be done; and the chemist, say, will find here matter which will attract his interest as a specialist, and essays which will tell him something of recent advances in physics and in biology. Seven lectures in the chemistry section, six in the natural history, and four in the physics section, complete an excellent bill of fare. The Royal College of Science has got in first, and members of other and more slow-going London Colleges can only wish them heartily, and yet perhaps a little enviously, good fortune and good voyage in their endeavour.

A. F.

Under the general heading "*Actualités Scientifiques et Industrielles*" we have received the monographs listed below. Each is written by an authority on his subject and the treatment is, in general, concise and clear. The publishers are Hermann et Cie., 6, Rue de la Sorbonne, Paris.

84. O. SCARPA. *Pile Metalliche*. 6 fr.
85. Prof. Dr M. VOLMER. *Das elektrolytische Kristallwachstum*. 4 fr.
86. F. BLOCH. *Les Électrons dans les métaux*. 5 fr.
87. A. F. JOFFÉ. *Conductibilité électrique des isolants solides et des semi-conducteurs*. 10 fr.
88. LÉON BRILLOUIN. *Les Électrons dans les métaux du point de vue ondulatoire*. 9 fr.
89. LÉON BRILLOUIN. *Conductibilité électrique et thermique des métaux*. 18 fr.
90. J. HEYROVSKY. *A Polarographic Study of the Electro-Kinetic Phenomena of Adsorption, Electro-Reduction and Overpotential, Displayed at the Dropping Mercury Cathode*. 12 fr.
91. RENÉ AUDUBERT. *Phénomènes photoélectrochimiques action de la lumière sur le potentiel métal-solution*. 8 fr.
92. A. GILLET et N. ANDRAULT DE LANGERON. *Les Colloïdes et la couche de passage*. 10 fr.
93. PAUL DUTOIT. *Sur le potentiel métal/solution*. 4 fr.
94. GEORGES BROOKS. *Laque d'Indochine*. 18 fr.
97. PHILIPP FRANK. *Théorie de la connaissance et physique moderne*. 10 fr.
98. P. SWINGS. *La Fluorescence des molécules diatomiques*. 10 fr.
99. P. SWINGS. *La Fluorescence des molécules diatomiques-phénomènes complexes*. 10 fr.
105. M. PRETTRE. *L'Inflammation et la combustion explosive en milieu gazeux*. 15 fr.
107. JEAN ULLMO. *Les Idées d'Eddington*. 7 fr.
110. JEAN-J. TRILLAT. *Les Preuves expérimentales de la mécanique ondulatoire*. 12 fr.
112. Sir ARTHUR EDDINGTON. *Sur le problème du déterminisme*. 6 fr.
121. E. DARMOIS. *Un nouveau corps simple: le deutérium ou hydrogène lourd*. 7 fr.
122. G. MALFITANO et M. CATOIRE. *Les Composés micellaires selon la notion de complexité croissante en chimie*. 9 fr.
130. CARL BENEDICKS. *Nouveaux résultats expérimentaux sur l'effet électro-thermique homogène*. 8 fr.

131. LOTHAR NORDHEIM. *Die Theorie der thermoelektrischen Effekte*. 6 fr.
132. PAUL LANGEVIN. *La Notion de corpuscules et d'atomes*. 12 fr.
140. JEAN-LOUIS DESTOUCHES. *Les Principes de la mécanique générale*. 15 fr.
143. M. GEORGES BOULIGAND. *Relations d'incertitude en géométrie et en physique*. 9 fr.
152. MORITZ SCHLICK. *Les Énoncés scientifiques et la réalité du monde extérieur*. 10 fr.
153. LOUIS LEPRINCE-RINGUET. *Rayons cosmiques: aspect des phénomènes et méthodes expérimentales*. 15 fr.

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AN X-RAY STUDY OF THE EFFECT OF HEAT ON THE STRUCTURE OF SPUTTERED FILMS OF GOLD

By S. RAMA SWAMY, B.Sc., PH.D., The Indian Institute of
Science, Bangalore, India

Received April 7, 1934.

ABSTRACT. Sputtered films of gold of different thicknesses were heated to various temperatures up to 800° C. and their Debye-Scherrer photographs were obtained after each stage of heating. The photographs showed on examination that on being heated the gold crystals in the film oriented themselves in such a way that their 111 planes were parallel to the surface of deposition. The crystals were also found to grow when the film was heated. The degree of orientation as well as the size of the crystals, obtained from the photographs, were found to depend on both the thickness of the film and the temperature to which it was heated.

§ 1. INTRODUCTION

IN an earlier paper on the transmission of light by thin films of metal* it was observed that sputtered films of gold break up into aggregates, separated from each other, on being heated. Kahler† and G. P. Thomson‡, who examined sputtered films of metals, observed them to consist of minute crystals oriented at random. G. P. Thomson, Norman Stuart and C. A. Murison§, who worked with sputtered films of platinum, noticed that in some of them the crystals exhibited orientation phenomena. Trillat and Hirsch|| observed a development of fibre structure on heating thin beaten leaves of platinum and gold. The present work was undertaken to investigate whether similar phenomena are exhibited by sputtered films of gold when heated, X-ray diffraction methods being employed for the purpose.

§ 2. PREPARATION OF THE GOLD FILMS

The gold films used were sputtered on thin rods of quartz about 2.5 cm. long and 0.9 mm. in diameter in an apparatus which has been described in an earlier

* S. Rama Swamy, *Proc. R.S. A*, 131, 307-20 (1931).

† H. Kahler, *Phys. Rev.* 18, 210-17 (1921).

‡ G. P. Thomson, *Proc. R.S. A*, 125, 352 (1929).

§ G. P. Thomson, Norman Stuart and C. A. Murison, *Proc. Phys. Soc.* 4, 381-87 (1933).

|| J. J. Trillat and T. v. Hirsch, *Z. f. Phys.* 75, 784-803 (1932). See also *Comptes Rendus*, 193, 649 (1931) and 194, 72 (1932).

paper*. The gold plate used as the cathode was 99.99 per cent pure. The quartz rod on which the film was sputtered was provided with suitable mica rests at its ends and laid on the table provided for it in the sputtering apparatus. In order to obtain a uniform deposit of gold the rod was first sputtered on one side and then turned over and sputtered on the other side for an equal interval of time under the same conditions of pressure and applied voltage. The apparatus was evacuated with a Hyvac pump and the requisite discharge for sputtering was produced by an induction coil with a mercury interrupter connected to the 110-volt d.-c. mains. A thermionic rectifier was used in the secondary circuit. The applied potential for sputtering was of the order of 20 kV. and the current was 5 mA. The time of sputtering varied from about 20 minutes to an hour. The pressure in the apparatus, the gas in which was residual air, corresponded to a dark-space length of 5 mm. and was kept constant by a pressure-controlling device described in a note elsewhere†.

The quartz rod was thoroughly cleaned by washing first with alcohol and then with boiling conductivity water. It was dried and weighed in an assay balance to an accuracy of within 0.02 mgm. Its diameter was measured with a micrometer microscope in at least three places along its length and then it was sputtered and weighed again. This enabled the thickness of the film to be calculated to an accuracy of 0.2×10^{-5} cm., assuming it to be uniform. Films of varying thicknesses were obtained by sputtering for different intervals of time under the same conditions of pressure, applied voltage and current-strength. The weights and thicknesses of the gold films prepared are given in table 1.

Table 1

Number	3	5	6	7
Weight (mgm.)	0.74	0.79	0.24	0.55
Thickness (cm. $\times 10^{-5}$)	5.8	6.2	1.8	4.4

§ 3. EXPERIMENTS WITH THE FILMS

X-ray photographs of the gold films were obtained with a cylindrical Debye-Scherrer camera. A Müller X-ray tube with a copper anticathode was used and good photographs could be obtained in about 2 hours with 50 kV. and 10 mA. The heat treatment of the films consisted in maintaining them for about $4\frac{1}{2}$ hours at successively higher temperatures varying from 200 to 900° C. in an electric furnace. The maximum variation of temperature for each heat treatment was about 10° C. X-ray patterns were obtained after each heat treatment. With the help of identifying-scratches made on it, the film was always kept in the same position in the Debye-Scherrer camera so that in all cases the same portions of the film produced the patterns obtained.

* *Loc. cit.*

† S. Rama Swamy, *J. Sci. Inst.* 11, 28-29 (1934).

After heat treatment, intensity-maxima became noticeable in the central portions of the Debye-Scherrer rings of the 111 and 222 planes, indicating that the crystals in the film were oriented with their 111 planes parallel to the surface of deposition, figure 1. These maxima were found to get smaller and better defined at higher temperatures. The Debye-Scherrer rings also grew sharper when the films were heated, thus indicating crystal growth. Film 3 was found to exhibit the orientation even before being heated. In order to place the observations on a quantitative basis the lengths L of the maxima were estimated by visual measurements and also with the help of a recording photometer.

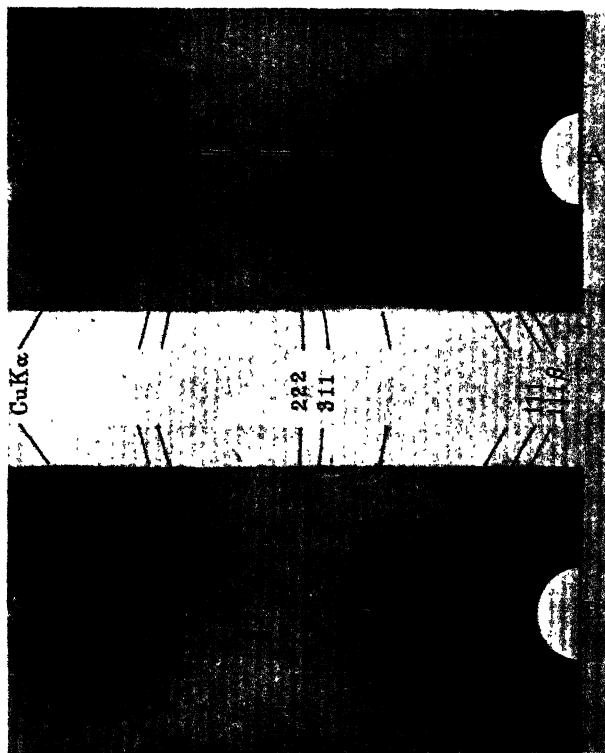


Figure 1. *A* is the Debye-Scherrer pattern of gold film no. 6 before heating. *B* is the pattern of the same film heated at 800° C. for 4½ hours. The two arrow marks in *B* indicate the intensity-maximum observed in the 111α ring. In the original photograph the maxima in 222α and 111β are also clearly visible.

The length of the intensity-maximum indicating *perfect* orientation of the 111 planes will be the same as the diameter of the incident X-ray beam, which is assumed to be parallel. When the X-ray beam is divergent, the corresponding length will be slightly more and can be calculated from a knowledge of the divergence of the beam and the diameter of the slit used. In the camera employed this length was 1.5 mm. If L is the measured length,

$$L_0 = L - 1.5,$$

where L_0 is the length of the maximum due to orientation of the crystals. If ϕ is the angle between the Bragg plane corresponding to either end of the maximum and the surface of the film at that point, it can be shown that

$$\tan \phi = L_0/(d \sin \theta),$$

where d is the camera diameter and 2θ is the angle of diffraction corresponding to that particular Debye-Scherrer ring. The angle ϕ is a measure of the departure from perfect orientation and will be zero for perfect orientation and $\pi/2$ when orientation is absent. In figure 2 the values of ϕ obtained from the photographs are plotted against the temperatures at which the films were heated.

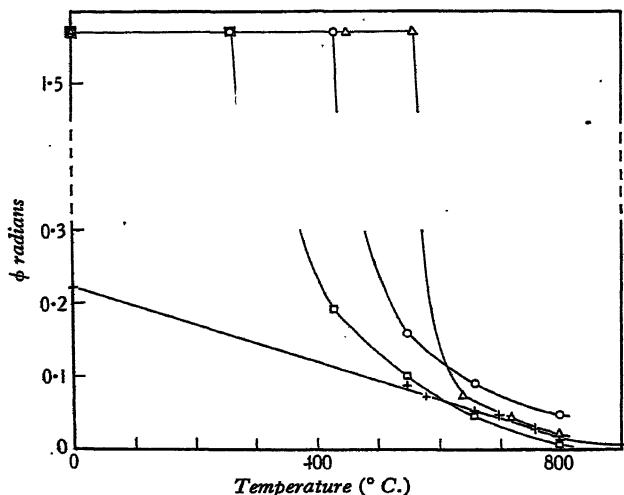


Figure 2. + Film no. 3; □ film no. 6; ○ film no. 7; △ film no. 5.

In order to study growth of the crystal when the gold films are heated, the half-intensity width of the 311 line in the photographs of films 6 and 7 was obtained from its photometer records. If D is the average length of the edge of the crystals taken as cubes, we have

$$B = b + k\lambda/(D \cos \theta)^*,$$

where

$$k = 2\sqrt{(\pi^{-1} \log_e 2)}$$

and

B is the measured, half-intensity angular width,

2θ the angle of diffraction,

b the part of B due to the finite size of the specimen, and

λ the wave-length of the X-rays used.

D will be in Ångströms if λ is in Ångströms, B and b being in angular measure. The values of D thus obtained are plotted against temperature in figure 3. The error in the measurement of the half-intensity linear width is about 0.01 mm. and so the calculated values of D are subject to an error of about 2 per cent.

* R. W. G. Wyckoff, *The Structure of Crystals*, p. 376.

§ 4. DISCUSSION OF RESULTS

The orientation phenomenon has been found in all the gold films examined. The curves in figure 2 indicate that the orientation becomes noticeable at a certain temperature and becomes more perfect on further heating. The temperature at which orientation becomes noticeable is lower for the thinner films than for the thicker ones. Thus, orientation was first noticed at 430°C ., 550°C . and 640°C . respectively for films of thicknesses 0.018μ , 0.044μ and 0.062μ respectively. This is possibly due to the existence of greater freedom in the thinner films, in which the crystals being farther apart than in thicker ones in which they are more closely packed. The curve for film 3, in which there was crystal orientation even before heating, is almost a straight line. Some platinum films examined by G. P. Thomson and his collaborators* exhibited a similar orientation even without being heated.

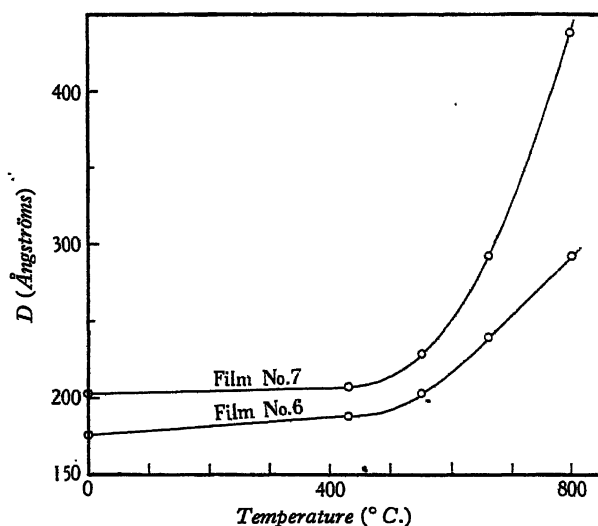


Figure 3.

The curves in figure 3 indicate that in addition to orientation there is also crystal growth when the films were heated. There is very little growth of crystals until about 400°C . But beyond this temperature they grow much faster with increase of temperature. The sizes of the crystals in films 6 and 7 are respectively 176 and 203 Å., the thicker film no. 7 containing the bigger crystals. Crystal growth is more pronounced in the thicker film than in the thinner one, the crystals being more than doubled in size at 800°C .

These two phenomena of crystal growth and orientation accompany the disintegration and consequent formation of aggregates mentioned in an earlier paper†. The lattice constant calculated from measurements of one of the photographs is

* *Loc. cit.*† *Loc. cit.*

4.07₁ Å., which is in good agreement with the value 4.0702 found by Sachs and Weerts*.

§ 5. ACKNOWLEDGMENTS

I take this opportunity to express my deep appreciation of the helpful interest which Prof. H. E. Watson has taken in this work. I must also thank Dr K. R. Krishnaswami for the many valuable suggestions which have considerably helped in its execution. My thanks are also due to Mr N. B. Bhatt for helping me to photometer the X-ray photographs.

* G. Sachs and J. Weerts, *Z. f. Phys.* **60**, 489 (1930). See also, Neuburger, *Z. f. Krist.* **80**, 114 (1931).

NOTE ON THE EQUALIZATION OF THE TEMPERATURES OF INTERFEROMETER TUBES

By J. J. MANLEY, M.A., D.Sc., Fellow of Magdalen College, Oxford

Received April 19, 1934.

ABSTRACT. This note is a description of two devices used for establishing and maintaining equality and uniformity of temperature for the contents of the twin tubes of Jamin interferometers. According to one method the tubes are closely wound from end to end with spirals of soft copper wire, s.w.g. 18. The other device consists of an aluminium chamber which during idle periods completely encloses the tubes. Shutters, covering the ends of the tubes, are removed prior to the carrying out of measurements.

At frequent intervals during the past two years, I have had occasion to carry out differential measurements of the continuous variations in the refractivity of benzene during intensive drying, and for the attainment of the required degree of accuracy it was imperative that the closest attention should be given to the conditions governing the temperature of the containing-tubes of the Jamin interferometer. Other workers in the field of interferometry must have experienced

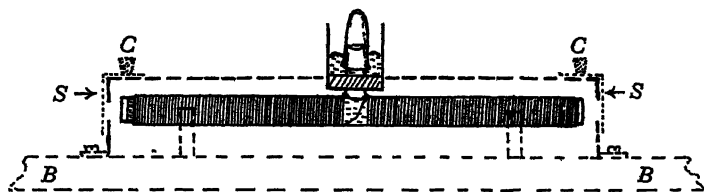


Figure 1. Note on the equalization of the temperatures of interferometer tubes.

difficulties similar to those encountered by myself, and I believe therefore that the two devices described below will be of interest to them.

So far as I am aware the glass tubes of an interferometer are usually placed *in situ* and left uncovered. Apparently the assumption is made that, given favourable conditions, corresponding and adjacent zones of the tubes have a common temperature; and that although the temperatures of the extremities on the left may differ from those on the right, the mean temperature of one tube is precisely equal to that of the other. Any uncertainty associated with such an assumption is, according to my experience, almost entirely removed by combining two devices which are represented in figure 1.

To the base *BB* of the interferometer is secured a rectangular aluminium chamber which in the figure is indicated by the heavier dotted lines. Apertures are provided in the lid of the chamber, as shown, for the passage of the tubulures

of the interferometer tubes. The circular windows at each end of the chamber are closed by the shutters *S, S* when observations are not being made. These shutters are provided with cork handles *C, C*. The interior of the chamber is blackened and the exterior polished. Experiments prove that such a chamber, by entirely screening the tubes from local and ever active air currents as well as from radiant energy, regular or otherwise, adds quite appreciably both to constancy and to accuracy.

Uniformity and equality in the temperature of the two interferometer tubes and their contents are still further increased by enveloping the tubes with tightly fitting spirals of copper wire as shown. The wire, no. 18 s.w.g., is wound not only tightly but also so closely that successive turns have contact with each other throughout. Thus the spirals, in their power of equalizing temperatures, approach in effectiveness to cylinders of copper; indeed their efficacy may in the present instance exceed that of copper tubes, because in the case even of the most closely fitting tube contacts between it and the enclosed glass chamber must necessarily be comparatively few; whilst the spiral, by adapting itself to the irregularities of the glass surface, is in contact throughout. Hence the conductivity of heat and the attendant equalization of temperature attain maximum values.

546.212:536.632

THE EFFECT OF DISSOLVED AIR ON THE SPECIFIC HEAT OF WATER

By R. JESSEL, A.R.C.S., PH.D., A.INST.P.

Received April 26, 1934 and is revised from June 9, 1934.

ABSTRACT. The paper describes experiments performed by the continuous-flow electric method on the specific heat of distilled water both when de-aerated and when saturated with air. The difference between the two sets of results is described and an explanation is given. The findings of other observers are critically described in the light of these experimental results.

§ 1. INTRODUCTION

IN his account of experiments on the specific heat of fractions obtained from petroleum oils* the writer noted that the true specific heat could only be obtained if the liquid was thoroughly de-aerated and that when the de-aeration was not complete results higher than normal were obtained.

The results obtained by numerous observers for the specific heat of water and its variation with temperature were examined and it was found that in nearly every case they were higher in value than the results of Callendar and Barnes; moreover, the latter observers took especial care to free their water from air. It occurred to the writer that the various discrepancies might easily be accounted for by the presence of dissolved air, and the present experiments were performed to test this hypothesis.

Callendar and Barnes decided to de-aerate their water primarily in order to obtain greater steadiness of temperature, having found that the liberation of air caused a certain amount of fluctuation in the temperature-rise. Below about 50° C., however, the fluctuations are slight because the air bubbles are very small, and the writer has been able, therefore, to obtain a series of results up to this temperature with ordinary distilled water. A second series of experiments was then performed with de-aerated water to see whether any difference could be observed and also whether the results of Callendar and Barnes could be reproduced.

The accuracy claimed for the writer's results on petroleum oils was 0.2 per cent, but if the discrepancies in the specific-heat measurements were to be explained much greater accuracy was needed since the differences between the findings of various observers were only of this order.

In the following sections the methods of obtaining the additional accuracy are described. The probable error in any individual experiment was not more than 0.02 per cent, but in combining two such experiments to give a value for the specific

* Lang and Jessel, *J. Inst. Petr. Tech.* 16, 783 (1930); 17, 572 (1931); 18, 850 (1932).

heat the probable error was somewhat increased. In any case, the results are certainly accurate to 0.05 per cent and, where more than two rates of flow have been taken, to at least 0.03 per cent.

§ 2. GENERAL OUTLINE OF THE METHOD

The principle of the method is to allow a stream of liquid to flow through a fine-bore glass tube, through which passes an electrically heated manganin strip, and to measure the rise in temperature arising from a steady supply of electrical energy. A very full discussion of the method has been given by Callendar and Barnes* in their classical papers on the variation of the specific heat of water with temperature.

References to the method and the apparatus used will be found in the papers of H. R. Lang† and of Lang and Jessel‡.

As frequent reference will have to be made in this paper to the work of these authors, this will be done by giving the author's name and the number of the page.

The elementary theory of the method is as follows:

If E is the potential-difference between the ends of the heater in volts,

C the current in amperes,

Q the rate of flow of liquid in grammes per second,

s the specific heat of the liquid,

J the mechanical equivalent of heat,

$d\theta$ the rise in temperature in degrees centigrade, and

h the rate of loss of heat in watts per degree of rise,

then when the conditions are steady the energy produced per second is

$$EC = JsQ d\theta + h d\theta \quad \dots\dots(1).$$

By changing the watts EC and the rate of flow Q in such a manner that the rise of temperature $d\theta$ is kept constant, two equations are obtained from which h can be accurately eliminated and s found. In practice it would be a long and tedious process to arrange for the values of $d\theta$ to be exactly the same in both cases, so values agreeing within 1 per cent are obtained and the equations are reduced as follows:

From equation (1)

$$Q_1 X_1 = JsQ_1 + h,$$

$$Q_2 X_2 = JsQ_2 + h,$$

where

$$X = EC/Q d\theta;$$

whence

$$s = (Q_1 X_1 - Q_2 X_2)/J (Q_1 - Q_2).$$

It is to be noted that h is assumed to be independent of both Q and $d\theta$; the necessary conditions for this have been carefully investigated and in these experiments great trouble has been taken to ensure that they were fulfilled; see § 8.

* *Phil. Trans. A*, 199, 55, 149 (1902).

† *Proc. R.S. A*, 118, 138 (1928).

‡ *J. Inst. Petr. Tech.* 16, 476 (1930).

§ 3. THE FLOW CIRCUITS AND CALORIMETERS

Both the liquid-flow circuit and the jacketing system were as used in the oil experiments and have been fully described by the writer. The only difference consists in the arrangement of the constant head and de-aerator and this is described in § 4. The two calorimeters used in these experiments are similar in all details, except for the size of the fine flow tube, to those described by Lang (p. 143).

The first calorimeter had a flow tube of $2\frac{1}{2}$ -mm. bore and the other one of 3 mm. The method of mounting the calorimeters has been fully described by Barnes (p. 204) and his procedure was adopted in the present investigation.

§ 4. THE DE-AERATOR

The de-aerating apparatus used in the final experiments is shown diagrammatically in figure 1. It acted very efficiently indeed, for when the water jacket of the calorimeter was heated to nearly 100° C. and water from the de-aerator was allowed to flow through the calorimeter no sign of even the smallest air bubbles could be seen in the emerging water.

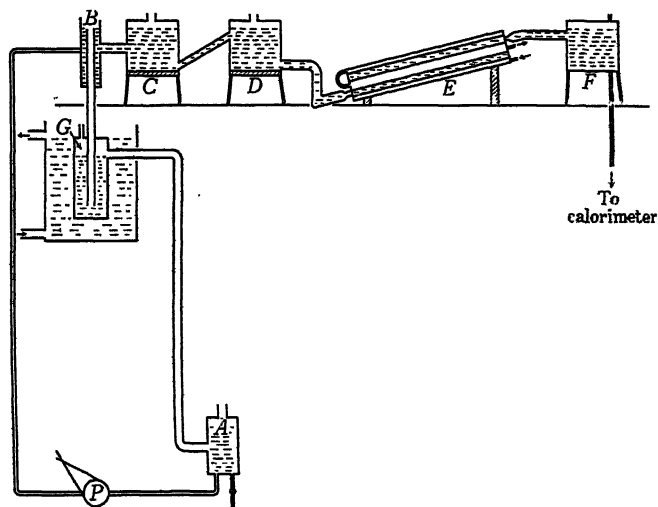


Figure 1.

Distilled water contained in the lower reservoir *A* was forced by means of a small rotary water pump into the overflow chamber *B*, which served to set the level of the water in the rest of the apparatus. This chamber was connected by a wide pipe, 1 in. in diameter, to the first heating-vessel *C*, which was a box 11 in. long, 4 in. wide and 4 in. high made from sheet copper and having a tight-fitting lid carrying three short funnels 2 in. long and $\frac{5}{8}$ in. in diameter. It was necessary to have an easy escape for the steam and the released air, otherwise the pressure set up became sufficiently great to drive the water back into the chamber *B* and so cause annoying fluctuations in head. The box rested on an electric fire element

11 in. long and 4 in. wide and capable of supplying about 1400 watts; in this chamber the water was heated to 95°C . and a great deal of air was released. The vessel *C* was connected to an exactly similar vessel *D* by means of two 1-in. tubes in parallel, water being taken off from the bottom of *C* and entering *D* just under the surface of the water. This second tank rested on a fire element which could supply about 1100 watts; in this vessel the water was completely and vigorously boiled and the remainder of the air expelled.

Water, now freed of air, was taken off from the bottom of the tank and cooled to room-temperature by flowing through the cooler *E*. This was designed to give a large surface area for cooling with the minimum restriction of flow. It consisted of three co-axial cylinders whose diameters were 1, $2\frac{1}{2}$ and 4 in. The hot water flowed through the annular space between the first two of these, while a fast stream of cold tap water passed through the smallest cylinder and also through the annular space between the last two. From the cooler the water passed into the last tank *F*, from which there was a take-off pipe to the apparatus proper; the water in this tank was covered with a layer of vacuum-pump oil to prevent contact with the air.

In order that the level of the water might be kept the same in all the tanks it was necessary to have everywhere the widest possible connecting-tubes. This caused further complications, for the hot water from *C* fed back into *B* and the overflow water became very hot; this heated the water in the reservoir *A*, which in turn heated the pump and caused it to leak badly and to function very poorly. To overcome this difficulty it was necessary to cool the overflow water. The wide overflow pipe was lead almost to the bottom of a wide cylinder *G* immersed in a large tank of cold water. When this vessel (*G*) became full, the water overflowed at the top back into the reservoir *A*. In this way it was possible to get a large area for cooling without slowing down the rate of pumping.

The interiors of the vessels *C*, *D*, *E* and *F* were all tinned with solder to prevent contamination of the pure distilled de-aerated water.

§ 5. MEASUREMENTS

Electrical measurements. The main heating circuit consisted of a battery of six 100-ampere-hour accumulators in series with an ammeter, a heavy manganin-wire standard resistance, a variable resistance board and the heater. By eliminating all rubbing contacts in the circuit it was possible to get extremely steady currents of any value up to about 5 A.

The power supplied to the heater was measured by determining the potential-difference between the ends of the standard resistance and between the ends of the heater in terms of Weston cadmium cells by means of a four-dial potentiometer. The various potential-readings were taken in rapid succession, by changing a single connecting-piece in suitably arranged mercury cups in a bakelite block.

The potentiometer was tested by taking its reading against one, two, three, four and five standard cells in turn when a 6-volt battery was connected across it.

The scale was found to be linear to at least 1 part in 5000. The standard cells were checked several times against three standard cells which had been calibrated at the National Physical Laboratory, and were found to agree with them to at least 1 part in 10,000. The value adopted in calculating the results of these experiments was

$$E = 1.0183 - 0.00004 (t - 20) \text{ international volts,}$$

correction being made for temperature at each reading.

The standard resistance, which was specially designed to carry heavy currents, consisted of a coil of bare manganin wire 3 mm. in diameter, wound non-inductively on a cubical frame of bakelite of about 15 cm. side and immersed in a water-cooled oil bath. This coil was standardized against a platinum silver coil calibrated at the National Physical Laboratory. The value adopted for the calculation of the results was

$$R = 0.9957 \pm 0.0005 (t - 20) \text{ international ohms,}$$

correction being made for temperature at each reading.

Thermometry. The rise in temperature of the water was measured to 0.001° C. by means of a single differential reading of a pair of platinum thermometers having a very nearly equal fundamental interval and connected to a Callendar-Griffiths bridge. The bridge was carefully calibrated both before and after the series of experiments, and the relative values of the coils did not change by more than 1 part in 5000. It should be noted that as the bridge wire had to be read to 0.05 mm. it was necessary to calibrate the bridge-wire very carefully.

The change in the value of the bridge-wire correction during the course of the experiments amounted to 1 part in 500, but is not likely to affect the first set of results (ordinary distilled water) as the experiments were performed immediately after the first calibration. In the second set of experiments the bridge-wire reading was never more than 2 cm., so that the error introduced is at most 0.004 cm. in a rise of 20 cm., which is about 1 part in 5000.

Three thermometers were used in these experiments. Thermometer A was used throughout as the outflow thermometer, as in the oil experiments. The inflow thermometer B used in those determinations gave considerable trouble owing to faulty insulation: it was repaired and used for a few of the earlier experiments, but it again gave trouble and was replaced by another thermometer E. The fundamental intervals and the ice points of these thermometers were taken before and after the series of experiments and are given in the table below, as are also the values of d determined at the end of the series. These were found from a measurement of the resistance of the thermometers in the vapour of boiling sulphur, the temperature t on the international scale being expressed by the relation

$$t = 444.60 + 0.0909 (p - 760) - 0.000048 (p - 760)^2,$$

where p is the atmospheric pressure in mm. An iron vessel and one tin shield were used as required by the definition of the international temperature scale.

It should be noted that the change in the ice point of thermometer A has no effect on the results, since only the fundamental interval of this thermometer enters into the calculations. The constants of the inflow thermometer only enter into the calculation of the mean temperature of the experiments and the small changes

noted above have no effect on the results. The values of d are higher than those usually given in text-books of physics, but the values agree favourably with those obtained by Lang for these thermometers some years ago, so they may be taken as substantially correct. No determination of d was made for thermometer B, but as this was made at the same time and with the same wire as for A the same value of d has been taken.

Table 1. Constants d of the thermometers

	Ice point (bridge units)	Fundamental interval	$d \times 10^{-4}$
Thermometer A (before)	1285.46	499.43	—
Thermometer A (after)	1284.70	499.40	1.56
Thermometer B (before)	1292.58	501.2	—
Thermometer E (before)	1283.76	499.63	1.57
Thermometer E (after)	1286.60	499.46	—

By taking differential readings before the current was switched on (cold readings), all other conditions being the same (Barnes, p. 195), corrections for conduction losses and for heat generated in the fine-flow tube by internal friction are eliminated. The only correction remaining is for the extra conduction from the outflow end of the calorimeter due to the rise in temperature. But as this increase is only 4°C . and as the end is carefully lagged, the correction must be vanishingly small.

The temperature-rise, having been obtained on the platinum scale, was reduced to the international temperature scale by means of the well-known formula

$$t - pt = d \times (t) (t - 100).$$

Corrections were made in the first place from the values tabulated by F. E. Hoare*, who uses a value of d equal to 1.5×10^{-4} , and were afterwards corrected for the values of d found by experiment.

Determination of weight. At the commencement of a run the water was collected in a previously weighed flask by switching over the special two-way tap (Lang, p. 145). It was found to be impossible to adjust the stops on the two sides of the tap to give exactly the same flow, so the following procedure was adopted. About 5 minutes before the run was due to commence, a spare flask was placed under the collecting side of the tap and conditions were allowed to become steady. 15 seconds before the start the tap was switched on to the other side, the weighed flask was substituted for the spare one and at the correct instant the tap was switched back again.

Evaporation during collection was prevented by a cardboard disc placed round the nozzles of the tap and fitting tightly over the neck of the flask. Except when under the tap they were kept tightly corked. The extent of possible evaporation was examined by leaving a collecting flask uncorked for 24 hours, and the loss of weight was less than $\frac{1}{2}$ gm. in a litre.

In the earlier experiments short runs were taken and flasks containing up to about 300 gm. were weighed on a chemical balance with calibrated brass weights.

* *J. Sci. Inst.* 6, 99 (1929).

In the later experiments when runs of 1000 sec. were taken about 1200 gm. were collected, and the flasks were weighed on a special large balance which was capable of detecting a change of 0.1 gm. when there was over 5000 gm. on the scale pans. The weights used were carefully scraped until they were of the correct value. A small correction was applied to reduce the weighings to those *in vacuo*.

Determination of time. For the short runs of the earlier experiments the time was recorded on a chronograph. Metal contacts were fixed to the arm of the two-way tap and to its stops, so that the time of changing over could be recorded. The chronograph drum was at the same time marked in seconds by a relay working off the pendulum of the standard clock in an adjacent astronomical laboratory. The rate of this clock was slightly variable, but the error was never more than 5 sec. in 24 hours, so that no correction had to be applied. Unfortunately the clock began, shortly after this, to give trouble by frequently stopping. As it was seen that the error in switching over and back at given signals was usually of the order of 0.1 sec. and never exceeded 0.2 sec., it was decided to take long runs of 1000 sec. and to start and stop the flow by counting the last 5 sec. with the tick of a chronometer and rapidly switching over at the given instant. An Arnold and Dent ship's chronometer was used for these time-determinations and it was rated against the broadcast Greenwich time signals. The rate was found to be constant and the error extremely small, only $2\frac{1}{2}$ sec. in 24 hours. The time-measurements are not likely to be more in error than 1 part in 5000.

§ 6. PROCEDURE

The method of making an experiment has been fully described by Lang (p. 147) and was adopted in this investigation. The temperature control of the thermostat, however, was much more satisfactory, all the heaters used were electrical, and errors due to fluctuations of gas pressure were thus eliminated. It was found possible to obtain quite steady conditions at any required temperature between 0° and 100° C.

In all cases the rise of temperature of the second and third rates of flow was so adjusted as to give the same mean temperature of experiment as the first flow.

§ 7. THE X TESTS

The elementary theory of the method (p. 748) assumes that the heat-loss h per degree is independent of both $d\theta$ and Q . But this assumption will hold only so long as the flow is turbulent, i.e. so long as there is proper mixing around the thermometers and stream-line motion is absent in the calorimeter. Since this fact is of vital importance for the success of the experiments, it was thought necessary to test the point experimentally. To this end three or four rates of flow were used on various occasions and the values of X obtained plotted against the values of Q^{-1} .

Now
$$EC = J_s Q d\theta + h d\theta,$$

where $d\theta$ is measured from an arbitrary zero given by the cold readings.

Then
$$\frac{EC}{Q d\theta} = X = J_s + \frac{h}{Q}.$$

If then h is independent of Q throughout the range of flows used, a straight-line graph will be obtained the slope of which gives the value of h while its intercept gives the value of the specific heat in work units.

In most of the experiments with ordinary distilled water three or four rates of flow were used, and some of the X graphs are shown in figure 2. It will be seen that the points lie on the straight lines to within 1 part in 2000. The intercept was taken in these cases as the mean specific heat and the probable error was less than if only two rates of flow had been taken. The rates of flow that give turbulent motion having been determined, only two rates of flow were taken in the second set of experiments, which related to air-free distilled water.

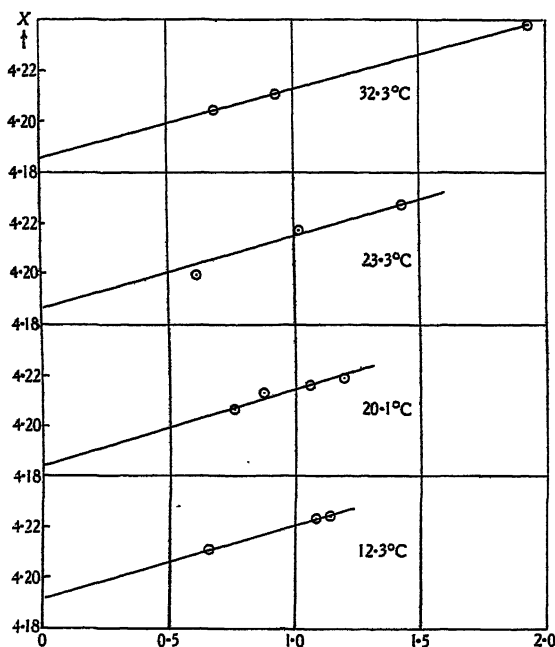


Figure 2.

Two other correcting factors may enter into the equations, one for the variation of temperature-gradient in the fine-flow tube (Callendar, p. 121) and one for the extra conduction from the outflow end of the calorimeter due to the rise in temperature. The latter correction has been regarded as negligible, an assumption which is now justified by the linearity of the X graphs.

The complete equation when corrected for the gradient in the fine-flow tube has been shown by Callendar (p. 124) to be

$$EC = JsQd\theta + h_0(1 + h_0/xJsQ - ad\theta/y)d\theta,$$

where x and y are constants while a is the temperature coefficient of the material of which the heater is made and in this case may be taken as zero for manganin.

Combining two such equations for two different rates of flow but the same rise of temperature $d\theta$ we get

$$\frac{E_1 C_1 - E_2 C_2}{d\theta (Q_1 - Q_2)} = Js - \frac{h_0^2}{x Js Q_1 Q_2},$$

and the correction for the specific heat in work units is $h_0^2/x Js Q_1 Q_2$. Further, Callendar has also shown that the value of $1/x$ is $11/25$. Taking values of 1.2 and 0.6 gm./sec. for Q_1 and Q_2 , and giving h_0 the high value of 0.06 W./deg., we find that this correction amounts to only 1 part in 10,000 of the final result and so can be safely neglected.

The effect of the gradient in the fine-flow tube would be to make the X graphs slightly parabolic. Examination of the curves, however, shows that the deviations are sometimes positive and sometimes negative; so they can be put down only to accidental and not to systematic errors.

§ 8. SUMMARY OF THE OBSERVATIONS

Table 2 gives a summary of the observations. Column I gives the inflow temperature reduced from the platinum scale by means of Hoare's tables ($d=1.5 \times 10^{-4}$), and it is the mean of the values obtaining at the beginning and end of the run. Column II contains the mean rise of temperature, reduced as above, and is the mean of readings taken every $\frac{1}{2}$ minute during a 5-minute run, or every minute during a 16-minute run or in reality a 1000-sec. run. Column III gives the energy supplied to the heater measured in international watts, and is the mean of potentiometer readings taken every $\frac{1}{2}$ minute or every minute for runs of 5 or 16 minutes respectively. Column IV contains the value of the rate of flow of water (gm./sec.) corrected for buoyancy as already explained. Column V shows the value of X calculated from the data given in the preceding columns. Column VI gives in work units the value of the specific heat corrected for the variation in the value of d , and for the value of the international watt in absolute units. This latter correction was made by adding 4 parts in 10,000 to the results, while the correction to the international scale of temperature was obtained from a graph drawn through the values of the correction at certain fixed temperatures. Column VII gives the mean temperature of the experiment while column VIII gives the value of h in watts per degree.

The value for the specific heat of air-free water at 50.2° C. was obtained with the use of a preliminary de-aerating system which was not so efficient as that used for all the other experiments. These results are shown graphically in figure 3. The smooth graph drawn through the values for air-free distilled water is that given by Barnes and corrected as described in § 10. It will be seen that the present results agree with those of Barnes to 1 part in 2000, which is the experimental error.

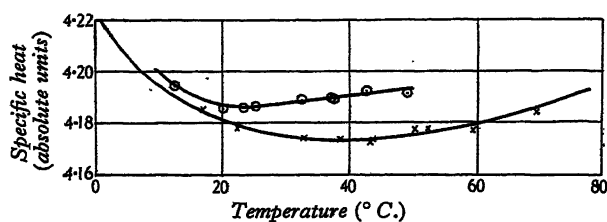


Figure 3. ○ ordinary distilled water; × de-aerated distilled water.

Table 2. Summary of results

Ordinary distilled water

I	II	III	IV	V	VI	VII	VIII
10.72 10.80 10.86	3.0340 3.0089 2.9915	19.267 11.147 11.461	1.5081 0.8770 0.9202	4.2111 4.2241 4.2233	4.1944	12.3	0.029
18.19 18.28 18.27 18.27	3.7563 3.6746 3.6838 3.6878	18.236 14.677 20.562 13.024	1.1522 0.9473 1.3274 0.8371	4.2134 4.2164 4.2070 4.2192	4.1857	20.1	0.031
21.54 21.56 21.60	3.4840 3.5245 3.4664	24.080 10.421 14.410	1.6457 0.6996 0.9856	4.1998 4.2275 4.2176	4.1859	23.3	0.031
23.53 23.52	3.4275 3.4263	20.008 10.424	1.3894 0.7211	4.2027 4.2193	4.1861	25.2	0.025
30.53 30.70 30.64	3.4431 3.2487 3.2642	21.111 7.141 14.794	1.4584 0.5187 1.0765	4.2041 4.2372 4.2103	4.1890	32.3	0.027
34.90 34.91 34.91 34.92	4.5516 4.5631 4.5376 4.5551	23.611 23.603 12.648 12.645	1.2346 1.2310 0.6612 0.6588	4.2018 4.2019 4.2158 4.2134	4.1893	37.1	0.018*
35.51 35.51 35.54 35.54	4.3597 4.3861 4.3481 4.3625	22.718 22.679 11.615 11.601	1.2398 1.2315 0.6345 0.6310	4.2011 4.1988 4.2102 4.2146	4.1892	37.7	0.016*
39.65 39.62	5.5837 5.7206	23.550 12.116	1.0016 0.5006	4.2107 4.2313	4.1924	42.5	0.024
46.86 46.85 46.83 46.83	4.3556 4.3820 4.3724 4.3838	23.167 23.152 8.726 8.717	1.2646 1.2558 0.4712 0.4700	4.2071 4.2061 4.2350 4.2307	4.1916	49.0	0.0201*

* Results obtained with the first calorimeter of bore $2\frac{1}{2}$ mm.

Table 2 (cont.)

De-aerated distilled water

I	II	III	IV	V	VI	VII	VIII
14·93 14·93	3·7490 3·7174	18·161 9·612	1·1458 0·6091	4·2164 4·2458	4·1858	16·8	0·038
20·23 20·33	3·6754 3·6300	18·270 9·590	1·1817 0·6341	4·2067 4·2333	4·1780	22·1	0·036
31·07 31·09	3·7023 3·5814	19·136 10·029	1·2265 0·6591	4·2141 4·2490	4·1740	32·9	0·051
36·79 36·88	3·6259 3·5832	19·072 9·947	1·2496 0·6543	4·2093 4·2424	4·1732	38·6	0·045
41·76 41·93	3·8273 3·7385	18·343 10·133	1·1384 0·6394	4·2100 4·2391	4·1724	43·7	0·047
42·08 42·10	3·6317 3·6477	18·140 9·549	1·1869 0·6173	4·2084 4·2404	4·1736	43·9	0·041
48·25 48·24	4·0397 3·9753	18·910 11·160	1·1070 0·6570	4·2287 4·2632	4·1776	50·2	0·056
50·59 50·71	3·7274 3·6895	18·415 9·699	1·1707 0·6175	4·2200 4·2575	4·1773	52·5	0·060
57·52 57·51	3·8615 3·9031	18·492 9·729	1·1364 0·5868	4·2141 4·2480	4·1772	59·5	0·039
68·04 67·92	3·4776 3·5785	18·356 9·717	1·2468 0·6346	4·2335 4·2792	4·1845	69·8	0·059

§ 9. DISCUSSION OF THE RESULTS

What is called the specific heat in this paper is really the average change in the total heat per degree centigrade. This definition takes into account the fact that some of the heat is necessary to increase the vibrational energy of the molecules, and some to cause internal changes in the substance, in addition to the small part used in expanding the liquid against the constant external pressure.

The particular shape of the (specific-heat, temperature) curve of the air-free water can be explained, as suggested by Callendar, by the presence in water of a number of both ice and steam molecules. At the lower temperatures there are many ice molecules and very few steam molecules, but as the temperature rises the number of ice molecules rapidly decreases while the number of steam molecules increases. When the temperature of the substance is increased, besides the heat that must be supplied to increase the energy of the molecules, a certain amount of internal latent heat must be supplied to melt the ice molecules and a further amount to form more steam molecules.

In figure 4 (*a*) these three factors are set out in a graphical form, the abscissae representing the temperature and the ordinates the absorption of energy per degree. The natural increase of the specific heat is shown as a line of positive slope, while the curves above this represent the energy necessary to get rid of solid

molecules and to form vapour molecules in solution. At 0°C . the energy required to melt the solid molecules is considerable, but as with rise of temperature the number of solid molecules present becomes less, the energy necessary to melt them becomes less and finally becomes zero. On the other hand there are practically no steam molecules present at 0°C . and so the contribution from this source is zero, but with rise of temperature the contribution to the total energy increases fairly rapidly because of the increase in the number of vapour molecules. In the uppermost curve the result of adding the ordinates at corresponding temperatures is shown, and it will be seen that the curve closely resembles the experimental one.

It must be noted that we speak of *steam molecules* in water and not of steam, for in de-aerated water bubbles of steam cannot exist. On the other hand when the water contains quantities of dissolved air the equation of a bubble of saturated air is

$$p + a/r^3 = P + 2T/r,$$

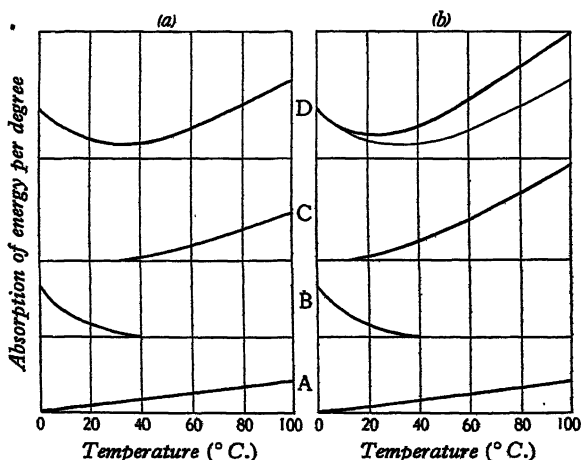


Figure 4. A, natural increase of specific heat; B, contribution of ice molecules; C, contribution of steam molecules; D, sum of A, B and C.

where a is a constant, T the surface tension, r the radius of the bubble and p , P the pressures outside and inside the bubble.

This is a stable condition when the radius is greater than $3a/2T$. As the temperature is raised the value of T decreases, so that the size of the smallest bubble that can remain in equilibrium in the liquid increases.

The air in the water then, will be in the form of small bubbles and these form numerous surfaces at which evaporation can take place; further, the total area of these surfaces rapidly increases as the temperature is raised.

The net effect on curve C, figure 4 (a), which shows the contribution due to vapour molecules, will be to make the curve steeper, and perhaps to make the effect of the vapour molecules reach measurable values at a lower temperature. The presence of air will not, however, have any effect on the contribution of the ice molecules or on the natural increase of the specific heat, so that the lower curves in figure 4 (b) will be the same as the corresponding curves in figure 4 (a). The result

of adding the ordinates at corresponding temperatures is again shown in the uppermost graph, and the specific heat shows higher values than in the corresponding curve in figure 4 (a) which is replotted in figure 4 (b). Further, we see that the minimum value occurs at a distinctly lower temperature.

Referring to the experimental results we see that the results for the specific heat of ordinary distilled water, which was probably saturated with air, are considerably higher than the corresponding results for air-free water, and also that whereas the minimum value for air-free water occurs at 37°C . the minimum value in the other case is at about 25°C . Our quantitative explanation appears to be on the right lines, but what seems to be most important is the fact that if *exact and reproducible results for the specific heat of water are to be obtained, air-free water must be used*. This is of the greatest importance because of the use of water as the standard calorimetric substance, and it is suggested that the calorie which is now defined as the quantity of heat required to raise the temperature of 1 gm. of water from 14.5° to 15.5°C . should for the most exact work be amended to read as the *quantity of heat required to raise the temperature of 1 gm. of air-free water from 14.5° to 15.5°C .*, for the difference caused by the presence of air may amount to 1 part in 1000.

Before passing on, a word or two about the heat-loss per degree as given in the last column of table 2 is perhaps necessary. It will be seen that the value of h was much higher in the case of the second calorimeter, but this is to be expected since the larger size of the bore of the fine-flow tube gives a larger surface for radiation. It will also be noticed that in the second series of experiments the heat-loss for this second calorimeter considerably increased: prior to these experiments, however, the calorimeter was taken up to over 90°C . several times in order to test various de-aerating systems, and the liberation of gas occluded on the walls will account for the rise in the heat-loss. The fact that the heat-loss depends on the previous history of the calorimeter was also noticed by Barnes. It should be noted that the largest heat-loss was only 1 per cent of the heat supplied in the case of the fast flows and about 2 per cent in the case of the slow flows.

It is perhaps advisable to stress the fact that the results for the specific heat are expressed in absolute units (joules) and on the international scale of temperature.

§ 10. THE RESULTS OBTAINED BY OTHER OBSERVERS

If the results obtained by other observers are to be readily compared it is necessary to reduce them to a set of common units, and it seems obvious that we should choose absolute units (joules) and express temperature on the international scale.

Barnes was, as far as can be ascertained, the only experimenter who took the precaution of freeing the water from air. His results have to be corrected for the e.m.f. of the Clark cells (whose value he took as 1.4342 international volts) and for the international ohm. King* has shown that the e.m.f. of the Clark cells was, as Barnes suspected, 1.4325 international volts, which is equivalent to 1.4335 absolute

* See Callendar, *Phil. Trans. A*, 212, 8 (1912).

volts. The values thus corrected are shown in the third column of table 3, Barnes's original results being given in the second column.

No correction for the temperature scale is necessary since the value of d was obtained on the assumption that the boiling-point of sulphur is 444.53°C. , which is near enough to the value 444.60°C. on the international scale as to make no difference.

Barnes neglected to make any correction for the temperature-gradient in the fine-flow tube (shown to be negligible in the present experiments) but the correction has been carefully worked out by Callendar (p. 129) and has here been added to Barnes's results, the final corrected values being given in the last column of table 3.

Table 3. Correction of Barnes's values of specific heat of water

Temperature ($^{\circ}\text{C.}$)	Specific heat as given by Barnes (joules)	Corrected for adjustments of electrical units	Corrected for temperature- gradient in fine-flow tube
5	4.2105	4.2045	4.2050
10	4.1979	4.1919	4.1924
15	4.1895	4.1835	4.1842
20	4.1838	4.1778	4.1786
25	4.1801	4.1741	4.1750
30	4.1780	4.1720	4.1731
35	4.1773	4.1713	4.1726
40	4.1773	4.1713	4.1727
45	4.1782	4.1722	4.1738
50	4.1798	4.1738	4.1756
55	4.1819	4.1759	4.1779
60	4.1845	4.1785	4.1807
65	4.1870	4.1810	4.1834
70	4.1898	4.1838	4.1864
75	4.1925	4.1865	4.1893
80	4.1954	4.1894	4.1921
85	4.1982	4.1922	4.1955
90	4.2010	4.1950	4.1986
95	4.2038	4.1978	4.2017

As recently as 1921 a very accurate set of determinations of the specific heat of water between 0° and 50°C. was performed by Jaegar and Steinwehr*, who used the electrical method of heating. The smallness of the rise of temperature used was not an advantage, for it meant that temperatures had to be read to 0.0002°C. and this is extremely difficult, if not impossible when the temperature is rising. Moreover, the difference between the specific heat at $t^{\circ}\text{C.}$ and the mean specific heat over a range of 8° or 10°C. about t is less than 1 part in 10,000. Thus the use of a small rise makes measurement more difficult and has no compensating advantage.

The results were expressed on the hydrogen scale, which between 0° and 100°C. is near enough to the international scale, and in terms of the international electrical standards. The corrected results are shown in table 4.

It will be seen that, except at the lowest temperatures, the results obtained by other workers are considerably higher than those obtained by Barnes, and whereas

* Jaegar and Steinwehr, *Ann. d. Physik*, 64, 305 (1921).

Table 4. Specific heat of water according to various observers

Temperature (° C.)	Barnes	Jaegar and Steinwehr	Hercus and Laby	Rowland	Griffiths	Bousfield and Bousfield
5	4·2050	4·1987	—	—	—	—
10	4·1924	4·1918	—	4·192	—	4·1872
15	4·1842	4·1863	4·1860	4·184	4·184	—
20	4·1786	4·1821	4·1809	4·179	4·179	4·1771
25	4·1750	4·1792	—	4·176	4·175	—
30	4·1731	4·1776	—	4·173	—	4·1767
35	4·1726	4·1774	—	4·173	—	—
40	4·1727	4·1785	—	—	—	4·1832
45	4·1738	4·1803	—	—	—	—
50	4·1756	—	—	—	—	4·1936
60	4·1807	—	—	—	—	4·2049
70	4·1864	—	—	—	—	4·2143
80	4·1921	—	—	—	—	4·2188

the latter found a minimum value at 37·5° C., Jaegar and Steinwehr find it somewhere between 30° and 35° C. It is suggested that this difference is due to the presence of dissolved air in the water. Jaegar and Steinwehr's values of the specific heat are not, however, so high as those obtained for ordinary distilled water, nor is their minimum at so low a temperature. It is therefore probable that Jaegar and Steinwehr used either freshly distilled water or water that had been previously boiled so that it was in part de-aerated. It is important to note that the liberation of air in a large calorimeter of the type used by them would not affect the steadiness of the conditions, so that the accuracy of the measurement would not be diminished.

The only other recent experiments on the specific heat of water were those of Hercus and Laby*, but these extended over only a very small range of temperature from 15° to 20° C. The results obtained were 4·1860 at 15° C., and 4·1809 at 20° C.; the accuracy claimed was 1 part in 10,000. The corresponding values of Barnes (corrected) are 4·1842 and 4·1786, the differences amounting to 5 and 6 parts respectively in 10,000. Although Hercus and Laby mention that no air was released in the apparatus, no special de-aeration was effected by them and the water must have contained small quantities of dissolved air, which would account for their higher values.

Of the older experiments probably the most accurate were those of Rowland. Day† restandardized his mercury thermometers and reduced the temperatures to

* *Phil. Trans. A*, 227, 63 (1927).

† *Phil. Mag.* 48, 1 (1898).

the hydrogen scale. Some doubt must still rest upon these results, however, for it was not possible to standardize the thermometers under the experimental condition of a rapidly rising temperature. The corrected results are given in table 4.

The agreement between the two sets of results is remarkably close. Rowland did not use de-aerated water, but violent agitation is an effective means of getting rid of air and it is probable therefore that the churning up which the water received in the calorimeter was the means of liberating a large proportion of the dissolved air. Rowland was not very certain of the minimum value at 30° C. and suggested that it might be higher, but from the results of the present experiments it seems likely that the low minimum point may have been due to the remaining quantities of dissolved air.

Griffiths* expressed his results in terms of the e.m.f. of the Clark cells (taken as 1.4342 V.), the standard ohm, and on the nitrogen scale. The true value of the e.m.f. of the cells is somewhat in doubt, for whereas Griffiths takes the value as 1.4323 V. or 1.4330×10^8 e.m.u., Laby† suggests that their value was probably 1.4336×10^8 e.m.u. Taking the smaller value so as to make the results as low as possible we obtain the values given in table 4, which are corrected for the electrical units and to the hydrogen scale.

It will be seen that the results are higher than those of Barnes by as much as 1 part in 1000, owing no doubt to the presence in the water of quantities of dissolved air. It is interesting to note that if the value of the Clark cells given by Laby are adopted the results agree very closely with the present values for ordinary distilled water.

The early experiments of Ludin‡ cannot be directly compared with those of the other observers so far mentioned because he used the method of mixtures and consequently was only able to obtain relative values of the specific heat of water. His results are interesting for they show a minimum value at 25° C. and a maximum value at 85° C. Between these two points the curve is very much steeper than that of Barnes but after the maximum has been reached it falls steeply until it has nearly the same value as that of Barnes at 100° C., the two curves being made to agree at 15° C.

Callendar§ has criticized these results and suggests that the drop in the curve near 100° C. can be readily explained by the slight loss of heat due to evaporation of the nearly boiling water on its way to the calorimeter. Although this may be the explanation it is by no means certainly so, for Bousfield and Bousfield|| obtained a curve whose shape was almost identical with that of Ludin.

The Bousfields' results are shown in table 4. Above the minimum value they are much higher than those of Barnes, and the difference is greater than can be ascribed to the many possible experimental errors. The minimum value occurs at 25° C. The shape of the curve can be satisfactorily explained if we suppose that the

* Griffiths, *Dict. App. Phys.* 1, 490 (London, Macmillan and Co.).

† Laby, *Proc. Phys. Soc.* 38, 169 (1926).

‡ Ludin, *Inaug. Diss. Zurich* (1895).

§ Callendar, "Bakerian Lecture," *Phil. Trans. A*, 212, 1 (1912).

|| Bousfield and Bousfield, *Phil. Trans. A*, 211, 199 (1911).

water was, as it must have been, saturated with air. This would account for the low temperature of the minimum, and the maximum value can be explained by the fact that above 80°C . a large proportion of the dissolved air is liberated. In an open calorimeter this could easily escape without affecting the steadiness of the conditions, and the results would then tend to resume their normal values, that is to say, the curve would tend to show a decrease in the specific heat with further increase in temperature.

The curves of Ludin and of the Bousfields are interesting in the light of the author's experiments on fractions obtained from petroleum oils. For fractions having initial boiling-points above 100°C . the (specific-heat, temperature) curves between 0° and 100°C . were all linear, but "fractions having initial boiling-points below 100°C . showed a curious bump" similar to the Ludin maximum at a temperature about 15°C . below the initial boiling-point. It was later shown that the peculiar shape was due to the presence of air or dissolved gas in the liquid, for when in later experiments better de-aeration was effected the graphs became exactly linear. There seems no doubt that the abnormal shape of the Bousfields' and Ludin's curves are due to a large extent to the presence of dissolved air.

The results obtained by the various observers mentioned in this section, except Ludin and the Bousfields, are not so high as those obtained for ordinary distilled water. It seems possible therefore that most of the observers started with freshly distilled or boiled water but took no precautions to prevent further contact with air. Only in a continuous-flow calorimeter is it possible to take this very necessary precaution. The differences found by various observers are not due to experimental errors so much as was previously supposed, but are due largely to the use by the various experimenters of substances which are not identical with one another.

THE ELECTRICAL CONDUCTIVITY OF STRONG ELECTROLYTES AND ITS VARIATION WITH TEMPERATURE

By C. J. B. CLEWS, B.Sc., A.Inst.P., East London College

Received May 9, 1934.

ABSTRACT. The electrolytic conductances of potassium sulphate, potassium nitrate and sodium sulphate have been measured over a wide temperature range by means of an accurate bridge method in which alternating current is supplied by a vacuum-tube oscillatory circuit. The sensitivity and accuracy of the method have been increased by using a suitably designed amplifying circuit, and special attention has been paid to the very important question of temperature-control during the experiments.

§ 1. INTRODUCTION

THE measurement of the electrical conductivity of electrolytes has attracted a great deal of attention from both physicists and physical chemists, and a large literature has accumulated round the subject. A search through the existing data, both in the standard books of physical constants⁽¹⁾ and in original papers, soon reveals, however, a lack of information as to the variation of this important property of solutions over a wide range of temperature.

Most investigators have satisfied themselves with a series of observations covering wide ranges of concentration at one particular temperature, generally 18° or 25° C. There are some notable exceptions such as the work of Noyes⁽²⁾, Jones⁽³⁾ and their collaborators who studied a number of electrolytes at temperatures as high as 306° and from 0° to 65° respectively. None of this work has been carried out, however, since the introduction of such improvements as thermionic valve oscillators giving alternating current of sinusoidal wave-form.

It was in view of this lack of data that the work was commenced at the suggestion of Prof. H. R. Robinson and Dr Allan Ferguson. S. J. Welton has already made a thorough investigation of aqueous solutions of potassium and sodium chlorides over a concentration range 0.1 *N* to 0.001 *N* at temperatures 18° and 25° to 85° C. at 5° intervals⁽⁴⁾; the present work extends the range of the investigations to uni-bivalent salts and a further uni-univalent salt.

§ 2. EXPERIMENTAL METHOD

Bridge. In the present investigation an improved form of the Kohlrausch apparatus⁽⁵⁾ was employed, a special Wheatstone network being assembled. A Cambridge ratio box (900-90-10-10-90-900) and a six-dial decade resistance box

provided three arms of the bridge; the conductivity cell formed the fourth arm. All bridge connexions were made with lead-covered cable, the outer covering of which was earthed.

Conductivity cells. Cells of many and varied patterns have been designed, but those designed by Washburn⁽⁶⁾ were selected as being most suitable in the present case, as air is completely excluded from them. These were made of Jena 16''' or pyrex glass and the electrodes were of stout platinum coated with platinum black.

Silence in the telephones depends on the instantaneous equality of potential at the terminals, which condition cannot be satisfied if the currents in the two branches of the bridge are out of phase. This difficulty is specially liable to arise, on account of the capacity of the cell, when one is dealing with electrolytes of high conductivity. To overcome it a variable condenser was connected in parallel with the decade box.

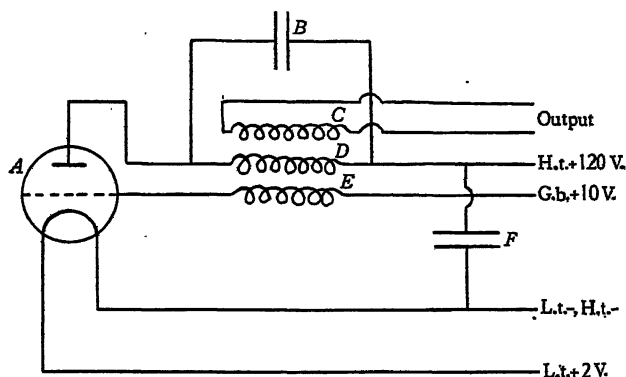


Figure 1. Oscillator. *A*, Osram P 215 valve; *B*, 0.27 mF. condenser; *C*, 1250-turn Igranico coil; *D*, 1250-turn Igranico coil; *E*, 1500-turn Igranico coil; *F*, 3-mF. condenser.

Alternating-current source. The Kohlrausch induction coil has been much used for this type of work, but the development of thermionic valve technique has led to the production of simple and entirely reliable substitutes which give a current of pure sinusoidal wave-form.

A one-valve oscillator of the tuned-anode variety was used in the present work giving a frequency of 1064 c./sec., figure 1.

Current-detector and amplifier. A pair of telephones *F* of the S. G. Brown type was used for the detection of the alternating current. The signals near the point of balance are generally exceedingly weak, with the result that a sharp minimum cannot be obtained. A two-stage amplifier was, therefore, inserted between the bridge and telephones, figure 2. Both the amplifier and oscillator were contained in earthed screening-boxes, and were far removed from one another.

Control and measurement of temperature. Temperature has a very appreciable influence on conductivity; the effect is about 2 per cent per degree centigrade, so that to obtain an accuracy of 0.1 per cent it is necessary to control the temperature to 0.05° C. Thus it is essential that a good thermostat should be employed. The cell was, therefore, immersed in a bath of liquid which was placed in an outer jacket, the space between these two containers being filled with wood wool. In

spite of the superior properties of water as a thermostat liquid, oil was used in view of the fact that there may be disturbing electrical effects with water⁽⁷⁾.

The temperature of the bath was controlled by a Lowry spiral regulator filled with aniline. A mercury contact operated a relay which switched the current through a 1200-watt Heatrae heater on or off. The oil was stirred vigorously by a motor-driven four-blade stirrer. This made it possible to control the temperature to within about 0.02°C .

The temperature was measured by means of a copper-constantan thermocouple in contact with the cell. In order to standardize the couple, the normal boiling-points of carbon tetrachloride, water, aniline and naphthalene were used as fixed points, the e.m.f. generated being measured on a thermocouple potentiometer reading to 1 microvolt and made by the Cambridge Scientific Instrument Co. The temperature was checked with a mercury-in-glass thermometer having a calibration certificate from the National Physical Laboratory.

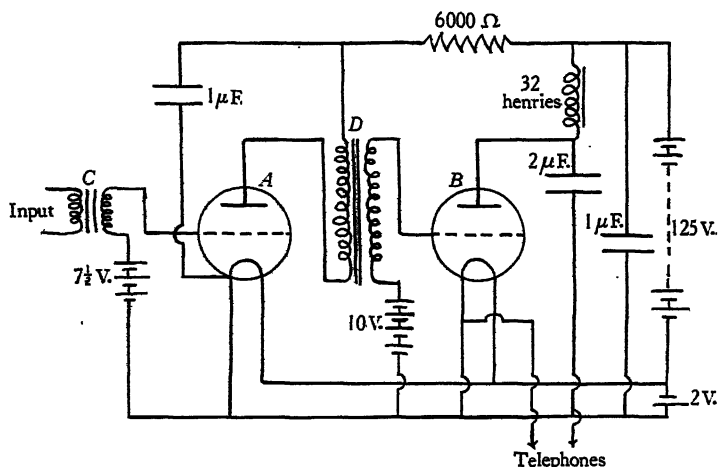


Figure 2. Amplifier. A, B, Osram P 215 valve; C, Varley transformer; D, Lotus inter-valve transformer.

Conductivity water. It is essential that the conductivity of the water used for making aqueous solutions of electrolytes should be as low as possible. A convenient and satisfactory apparatus for producing such water was described by Hartley and his collaborators⁽⁸⁾. Ordinary laboratory distilled water is boiled in a large tinned copper vessel of about 10 litres capacity; the steam passes into a block tin condenser, and only that which condenses on the central water-cooled tin tube is allowed to pass into a 3-litre pyrex flask, from whence it is siphoned for use. Water having a conductivity of 1 or $2 \times 10^{-6} \Omega^{-1}$ was obtained, and this is a convenient equilibrium value⁽⁹⁾, inasmuch as the water had been in contact with the air in the laboratory.

Solutions. The salts used, which were analytical reagents supplied by Baird and Tatlock or British Drug Houses, were recrystallized from conductivity water and thoroughly dried over phosphorus pentoxide in an air oven at 110 – 120°C . As

sodium sulphate exists in several hydrated forms it was treated rather differently. A quantity of an anhydrous sample was carefully weighed and was heated for 4 hours at about 120°C . On cooling, it was reweighed to test for loss of water of crystallization. No loss was detected and it was concluded that the sample was anhydrous.

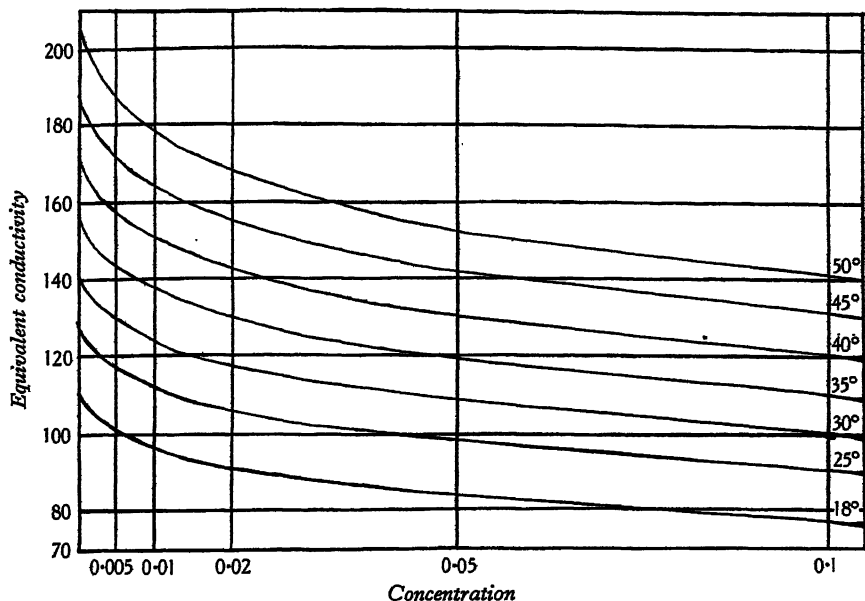


Figure 3. Equivalent conductivity of sodium sulphate.

The stronger solutions were made up by weight, the water as well as the salt being weighed. The weaker solutions were made up by diluting one of the stronger solutions. This operation was carried out in calibrated vessels. The cells were filled by means of a special pyrex flask. All glass apparatus used in preparing solutions

Table 1. Potassium sulphate 0.1 *N* (approximately). Cell type *B*

Temperature ($^{\circ}\text{C}$.)	R (Ω .)	Specific conductance $\times 10^3$	Concentration (gramme- equivalents per litre $\times 10^4$)	Equivalent conductance
18	282.83	0.9489	1.0009	94.81
25	244.77	1.0962	0.9993	109.7
30	222.80	1.2047	0.9979	120.7
35	204.50	1.3125	0.9961	131.8
40	188.59	1.4230	0.9944	143.1
45	174.85	1.5350	0.9925	154.7
50	163.24	1.6441	0.9903	166.0
55	152.62	1.7586	0.9880	177.9
60	143.48	1.8706	0.9854	189.8
65	135.31	1.9856	0.9828	201.9
70	127.95	2.0971	0.9800	214.0
75	121.32	2.2123	0.9770	226.4
80	115.32	2.3273	0.9740	238.9
85	109.93	2.4405	0.9708	251.4

was made of pyrex glass, and was thoroughly cleaned with chromic and sulphuric acid mixture. Distilled water and, finally, conductivity water were used for rinsing, the washings being tested with blue litmus paper.

Cell constants. The cell constants were determined by filling the cells with $N/10$ potassium chloride solution containing 7.4931 gm. of salt in 1000 gm. of conductivity water⁽¹⁰⁾. Parker and Parker's results for the specific conductivity were assumed⁽¹¹⁾. It can be shown that the temperature coefficient of the cell constant is very small, the variation over the range 18–85° C. being of the order 0.06 per cent. The constant was, therefore, determined at 18° and 25° and the mean value was assumed over the whole range, 18° to 85° C.

Table 2. Equivalent conductivity of potassium sulphate

Temp. (° C.)	0.05 <i>N</i>	0.02 <i>N</i>	0.01 <i>N</i>	0.005 <i>N</i>	0.001 <i>N</i>
18	101.68	110.1	115.86	120.12	126.7
25	118.0	128.1	134.2	139.4	148.0
30	129.8	141.5	148.1	153.7	165.8
35	140.8	155.1	163.3	168.9	183.6
40	153.2	168.8	179.1	185.0	200.0
45	166.5	182.5	194.2	202.3	218.3
50	180.1	196.2	210.1	218.1	236.7
55	193.4	210.1	226.5	232.7	252.5
60	207.0	224.2	239.8	249.7	269.7
65	220.4	239.2	258.4	265.8	286.2
70	234.4	253.5	273.6	282.0	307.6
75	248.4	269.5	291.0	300.6	327.3
80	262.5	284.8	308.2	317.5	346.2
85	276.6	301.3	324.6	336.5	367.2

§ 3. RESULTS

The results of the investigation of potassium sulphate, potassium nitrate and sodium sulphate solutions are shown in the accompanying curves and tables. It will be observed that, for a given concentration, the conductance of a solution increases with increasing temperature in every case. This is what we should expect from the Debye-Hückel-Onsager theory⁽¹²⁾.

We have

$$L = L_0 - (\alpha L_0 + \beta)\sqrt{(2C)},$$

$$\text{where} \quad \alpha = 5.78 \times 10^5/(DT)^{\frac{3}{2}}, \quad \beta = 58.0/(DT)^{\frac{1}{2}}\eta,$$

D is the dielectric constant,

T the absolute temperature,

η the viscosity of the solvent,

L the equivalent conductivity,

L_0 the equivalent conductivity at infinite dilution, and

C the concentration of the solution,

and it can be shown that α and β both increase approximately linearly with temperature. Welton⁽⁴⁾ has studied potassium and sodium chlorides, and his results

enable us to make a tentative calculation on the basis of the Debye-Hückel-Onsager theory. We can calculate α and β at various temperatures by consulting suitable tables for the dielectric constant and viscosity, and if we assume Welton's values for the conductance at infinite dilution at various temperatures we can calculate the conductance at any temperature and concentration. The result is shown in figure 5. At higher concentrations there is a wide difference between theory and observation,

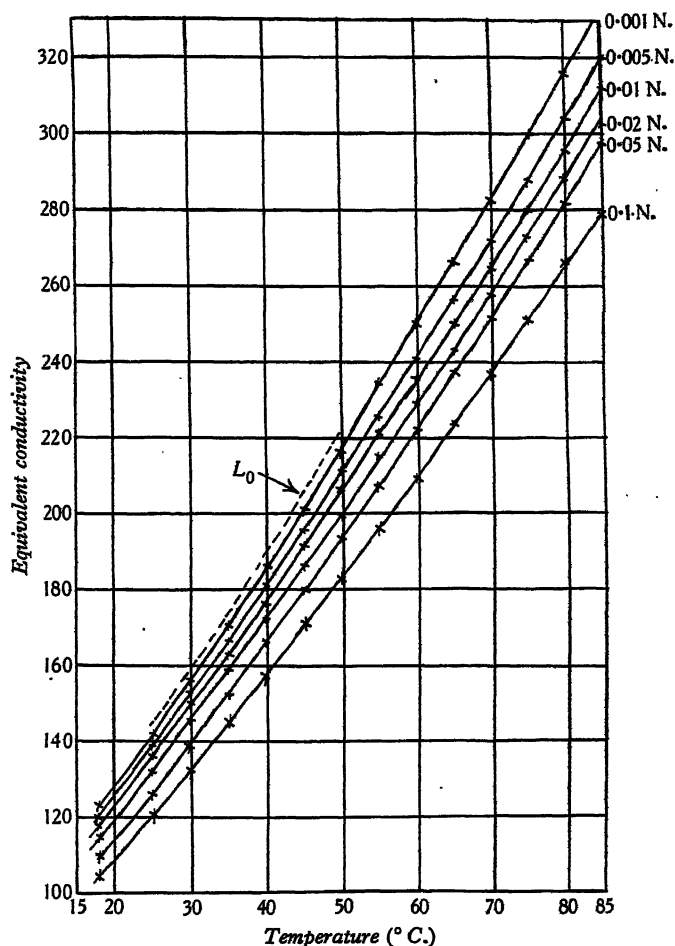


Figure 4. Equivalent conductivity of potassium nitrate.

but this is not surprising as the Debye-Hückel-Onsager equation is essentially a limiting equation. For concentration $N/1000$ agreement is strikingly good although there is a deviation (not shown) which the author attributes to errors in Welton's data at higher temperatures.

The Debye-Hückel-Onsager theory having been shown to hold at high temperatures, it can be applied with some degree of accuracy to calculate the conductance at infinite dilution of potassium nitrate by substituting the values of the

conductance for an $N/1000$ solution in the equation given above. The resulting values are shown in table 3.

Table 3. Conductance of KNO_3 at infinite dilution

Temp. °C.	25	30	35	40	45	50
L_0	144.5	159.0	173.8	189.7	205.4	221.3

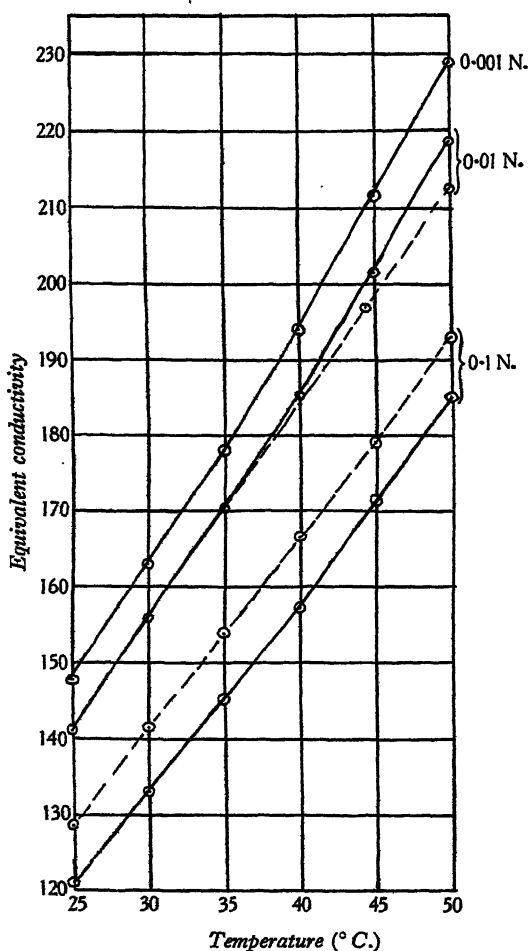


Figure 5. Equivalent conductivity of potassium chloride. —○— Debye-Hückel-Onsager theory. —○— S. J. Welton.

Unfortunately we are unable to apply the equation to the two uni-bivalent electrolytes, for it has not been put into a suitable form for application to higher-valence types.

An equation of much promise

$$L_0 = \frac{L + \beta\sqrt{(2C)}}{1 - \alpha\sqrt{(2C)}} - BC,$$

where, as before, C is the concentration and B an empirical constant, was proposed by Shedlovsky⁽¹³⁾.

It was valid for a number of uni-univalent electrolytes up to $N/10$ and, according to Shedlovsky, seemed to hold for uni-bivalent and salts of higher valency. Subsequent investigation has shown that the equation is not applicable⁽¹⁴⁾, and Shedlovsky hopes to devise an equation containing a term involving the logarithm of the concentration, predicted by Onsager.

In spite of the fact that previous workers on this subject have calculated values of the conductivity at infinite dilution the present author does not feel justified in doing so by falling back on any of the older methods of computing this constant, based on incomplete-dissociation theories such as Noyes's method⁽²⁾ or purely empirical equations of the type proposed by Ferguson and Vogel⁽¹⁵⁾.

§ 4. CONCLUSION

While the present investigation gives a fairly complete account of the change of electrolytic conductivity of three strong electrolytes with temperature in moderately concentrated solutions, correlation with theory is not possible until more extensive data on very dilute solutions are available. Nevertheless it seems that the Debye-Hückel-Onsager theory is fundamentally true and only requires a more rigid solution of the equations involved in the mathematical theory, or an empirical extension based on theoretical deductions. The author hopes to carry out some investigations of the conductivity of strong electrolytes in dilute solutions over a range of temperature in the near future, with an improved apparatus.

§ 5. ACKNOWLEDGMENTS

This work was carried out in the physical laboratories at East London College, and I have much pleasure in expressing my thanks to Prof. H. R. Robinson, F.R.S., for his advice and interest in the research and for the facilities which he has placed at my disposal.

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A NEW METHOD OF MEASURING THE ACOUSTICAL CONDUCTIVITIES OF ORIFICES

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Communicated by Dr E. G. Richardson, April 13, 1934.

ABSTRACT. The acoustical impedance of a tube driven by a loud-speaker is adjusted so that the acoustical pressure at a fixed point is zero. One terminating impedance is the orifice whose conductivity is required together with an adjustable tube, and from well-known impedance relations the conductivity can be calculated.

It is found that the conductivity C of a thin orifice of diameter d forming a constriction in a tube of diameter D is given by

$$C = 0.787d/(1 - d/D)^{1.895}.$$

When the orifices terminated the tube, the following relation was found to hold

$$C = d(1 + d/D)^{1.19}.$$

§ 1. INTRODUCTION

IT has long been observed that the acoustical conductivity of circular orifices placed at the end of a tube in which acoustic vibrations are being maintained is higher than that given by the classical theory. Recent work, notably that of G. W. Stewart* in America and E. G. Richardson† and E. J. Irons‡ in England has shown that the conductivity is in some cases many times greater than that required by theory. In the case of orifices acting as constrictions in a tube no theory has been offered.

The present work deals with a new method of measuring the conductivities of orifices terminating a tube and also with those forming constrictions.

§ 2. THEORY

The acoustical impedance Z_1 or Z_1' , defined as the ratio of alternating pressure to alternating volume-velocity, at any point P in a cylindrical tube is given by

$$Z_1 = (i \cos kl_1 \cdot Z_2 - R \sin kl_1) / \left(-\frac{1}{R} \sin kl_1 \cdot Z_2 - i \cos kl_1 \right) \quad \text{.....(1)}$$

looking towards the right, figure 1, and by a similar expression

$$Z_1' = (i \cos kl_1' \cdot Z_2 - R \sin kl_1') / \left(-\frac{1}{R} \sin kl_1' \cdot Z_2' - i \cos kl_1' \right)$$

* *Phys. Rev.* 27, 492 (1926).

† *Phil. Mag.* 7, 881 (1929).

‡ *Proc. Phys. Soc.* 40, 206 (1928).

§ Cf. Stewart and Lindsay, *Acoustics*, p. 138 (1931).

looking towards the left, where

Z_2 and Z_2' represent the terminating impedances to the right and left respectively,

$$i^2 = -1,$$

$k = 2\pi/\lambda$, where λ is the wave-length of the sound in air,

$$R = \rho c/S,$$

ρ is the density of air,

S is the area of cross-section of the tube,

c is the velocity of the sound in air, and

l_1, l_1' are the distances from P to the terminating impedances to the right and left respectively.

It is thus seen that the impedance at point P is determined by the values of the lengths l_1 and l_1' and the end impedances Z_2 and Z_2' . If the system is driven by a loud-speaker which forms part of the impedance Z_2' , a series of incident and reflected waves will be set up which, under certain circumstances, form a system of standing waves. The positions of the nodes and antinodes may be moved from point to point in the tube by altering the position or magnitude of the terminating impedances. By suitable adjustment of l_1 , therefore, P may be made a place of minimum pressure.

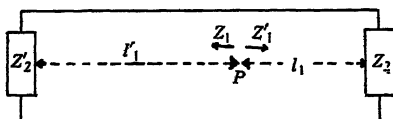


Figure 1.

If Z_2 is a rigid end and if l_1 is made equal to $n\lambda/4$, where n is any odd integer, the impedance looking to the right is zero. A microphone connected to a pressure-tube at P will record minimum sound but not necessarily silence. If the impedance Z_2' is now adjusted, it should be possible to obtain absolute silence in the telephones. Under these circumstances the impedance looking to the left also is zero.

On substituting an unknown impedance Z_2 in place of the rigid end and adjusting l_1 until silence is again obtained we have, from (1)

$$0 = i \cos kl_1 \cdot Z_2 - R \sin kl_1$$

or

$$Z_2 = -iR \tan kl_1 \quad \dots\dots(2).$$

Hence Z_2 is obtained in terms of l_1 .

The impedance to be measured consists of (a) an orifice forming a constriction in a tube, which is continued beyond the orifice to a rigid stop at a distance l_2 from it; or (b) an orifice terminating a tube.

In the first case the impedance consists of an orifice in series with a tube closed at one end. Hence

$$Z_2 = i\rho\omega/K - iR \cot kl_2,$$

where K is the conductivity of the orifice, ω is 2π times the frequency and $i\rho\omega/K$ is the impedance of the orifice.

The expression $-iR \cot kl_2$ is the impedance of the closed tube, obtained from equation (1) by giving Z_2 an infinite value. Substituting in equation (2) and putting $2\pi/\lambda$ for k we get

$$2\pi \frac{S}{\lambda K} = \left[\cot \frac{2\pi l_2}{\lambda} - \tan \frac{2\pi l_1}{\lambda} \right] \quad \dots\dots(3).$$

In the second case the impedance is that due to the orifice alone; hence

$$\begin{aligned} i\rho\omega/K &= -iR \tan kl_1 \\ K &= -\frac{2\pi S}{\lambda} \cot kl_1 \quad \dots\dots(4). \end{aligned}$$

The resistances of the orifices, due to viscosity and radiation, have been neglected since the smallest orifice used had a diameter of 0.5 cm. The resistance of the tube also has been neglected. The complete impedance of an orifice is given by

$$Z = \rho\omega k/2\pi + l(2\mu\rho\omega)^{\frac{1}{2}}/\pi r^3 + i[\rho\omega/K + l(2\mu\rho\omega)^{\frac{1}{2}}/\pi r^3]^*,$$

where r is the radius of the orifice and μ is the coefficient of viscosity. It is possible, therefore, to estimate the effect of the resistance. The first term is that due to radiation resistance if the sound waves emerge into free air, the second term is the resistance due to viscosity and the last two terms are the reactance components. At a frequency of 1000 c./sec. and for an orifice 0.5 cm. in diameter and 0.158 cm. long, we find the following values:

$$\frac{\text{Viscosity term}}{\text{Total reactance}} = 0.85 \text{ per cent}$$

$$\frac{\text{Total resistance}}{\text{Total reactance}} = 1.87 \text{ per cent.}$$

Where the orifice forms a constriction in the tube, the radiation resistance is absent and the latter ratio becomes 0.85 per cent. Since the viscosity resistance increases with frequency, a limiting frequency can be calculated above which it is not permissible to neglect the resistance.

§ 3. APPARATUS

Figures 2 and 3 show the apparatus used. A metal diaphragm loud-speaker L , driven by a valve oscillator and amplifier, is attached to one end of a brass tube 2 in. in internal diameter and about 18 in. long. At the other end is attached a brass connecting-piece C fitted with a short length of copper tube T called the "pressure-tube." This protrudes into the main tube and is bent so that the opening lies on and perpendicular to the axis of the main tube. Thus the position of the opening relative to any point in the tube can be accurately known. The faces of the connecting-piece are each capable of moving through about $\frac{3}{8}$ in. in a direction parallel to the axis but may be pressed back towards the main body of the connector against the tension of three spiral springs, as shown in figure 3. In virtue of this arrangement the main tube can be extended by a similar 2-in. tube or any other

* Cf. Stewart and Lindsay, *Acoustics*, p. 120 (1931).

apparatus whose impedance is required. The extension from the main tube is fitted with a massive brass piston *A* which can be moved to any position relative to the pressure-tube, the exact distance being measured by a metre stick *M* and the vernier *V* attached to the piston-handle. The piston consists of a solid brass cylinder 2 in. long having a $\frac{1}{4}$ -in. leather washer and a $\frac{1}{8}$ -in. brass plate at each end. It makes a good fit in the tube and side play is absent. Its impedance is therefore

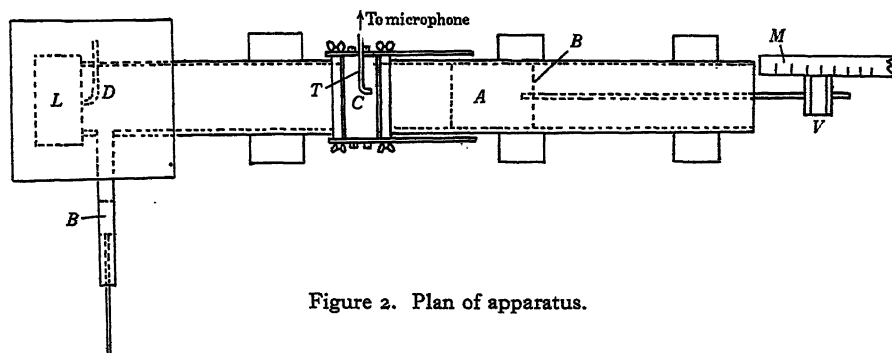


Figure 2. Plan of apparatus.

taken to be infinite. The pressure-tube communicates by means of a short length of rubber tubing with a telephone ear-piece acting as a microphone. It is placed in a metal box packed with cotton wool and mounted on rubber supports so that it is insulated from outside sound. The output is amplified by a 4-valve amplifier and

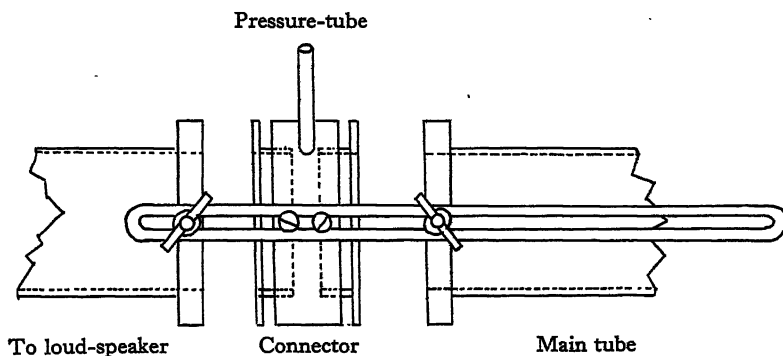


Figure 3. Detail of the connecting-piece showing the method of attachment to the main tube.

is listened to in head telephones. Similarly the loud-speaker is placed inside a metal box and cotton wool and felt are packed round it. Attached to the main tube near the loud-speaker are two side tubes; one $\frac{5}{8}$ in. in diameter, is fitted with a piston *B*, and the other, *D*, is $\frac{1}{8}$ in. in diameter and allows the pressure inside the tube to be restored to normal after any movement of pistons *A* or *B*.

The effect of the pressure-tube on the vibrations in the main tube was determined by separating the tubes at the connector as shown in figure 3, and using the main tube as a simple resonator excited by an external loud-speaker. Piston *A* was adjusted to give silence in a second microphone placed near the opening. It was

found that the introduction of the pressure-tube at any point in the main tube made no difference to the silence point; nor did altering the length of the rubber connexion from the pressure-tube to the microphone. Since the areas of the main tube and the pressure-tube were in the ratio of 256 : 1 little effect would be expected. From this it is seen that the pressure-tube and associated microphone were analogous to a voltmeter in an electrical circuit.

§ 4. PROCEDURE

In performing the experiment at any frequency, the apparatus was arranged as shown in figure 2 and piston *A* was moved through three or four successive positions of minimum sound in the headphones. These positions were noted and the wave-length of the sound was found by difference. The piston was now set at a distance of $\lambda/4$ cm. from the pressure-tube and piston *B* was adjusted to give silence in the head telephones. The impedance at the pressure-tube was therefore zero. It was found that the position of the piston *B* was rather critical, a movement of less than 1 mm. being sufficient to pass through a minimum. This adjustment had to be made for each frequency whether the orifices were to be measured in the tube or at the end of it.

Orifice within the tube. For this case the experimental orifice was inserted between the connecting-piece and the main tube and the piston *A* was adjusted to give silence once more. Three or four successive positions, differing by $\lambda/2$ from each other, were found so that the wave-length could be calculated. The experiments were repeated with the orifices moved to greater distances from the pressure-tube. This was effected by inserting a series of distance pieces, and a set of these was made up whereby l_1 could be increased to 8.75 in. in steps of 0.125 in.. Table 1 shows a typical set of results.

Table 1. A typical set of results

Diameter d of orifices (cm.)	Measured lengths l_2 (cm.)			$\lambda/2$ (cm.)	kl_2	$\cot kl_2$	$\frac{2\pi S}{\lambda K}$	K	
4.0	10.93	27.75	44.60	16.82	16.85	- 1.0976	- 0.5120	0.0752	50.3
3.5	10.44	27.92	43.98	16.85	16.69	- 1.1892	- 0.4013	0.1859	20.3
3.0	9.58	26.46	43.27	16.88	16.81	- 1.3502	- 0.2243	0.3629	10.7
2.5	8.19	25.02	41.46	16.83	16.44	+ 1.5316	+ 0.0392	0.6264	6.03
2.0	6.02	22.83	39.56	16.81	16.73	+ 1.1258	+ 0.4769	1.064	3.55
1.5	3.50	20.35	37.08	16.85	16.73	+ 0.8499	+ 0.8892	1.476	2.56
1.0	1.60	18.46	35.43	16.86	16.97	+ 0.2992	+ 3.242	3.829	0.986
0.5	0.46	17.34	34.16	16.88	16.82	+ 0.0860	+ 11.57	12.16	0.311

$l_1 = 13.96$ cm.; $kl_1 = - 0.5309$; $\tan kl_1 = - 0.5872$; mean of $\lambda/2 = 16.86$ cm.;
temperature 14.3° C.; $S = 20.2$ cm²; K is calculated from equation (3).

The conductivities of the orifices were obtained from equation (3) by plotting $\cot 2\pi l_2/\lambda$ against $\tan 2\pi l_1/\lambda$. The intercepts on each axis gave the values of $2\pi S/\lambda K$, from which K was calculated. It will be seen from figure 4 that the points

lie on a straight line except for large values of $\cot 2\pi l_2/\lambda$ and $\tan 2\pi l_1/\lambda$; for these the method ceases to be accurate.

These facts are illustrated in figure 5 where the conductivity is plotted against the distance l_1 of the pressure-tube from the orifice. When l_1 is small, i.e. when the orifice is at what corresponds to the first antinode, an abnormally large conductivity is obtained, which does not appear at the second antinode. This is due to the

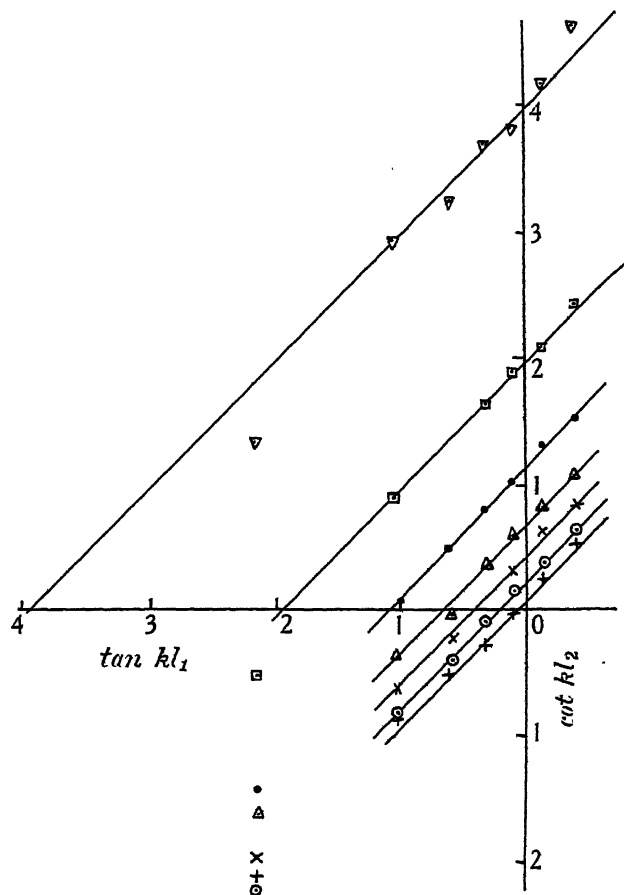


Figure 4. Orifices as constrictions in a tube. Graphs of $\tan kl_1$ against $\cot kl_2$ for the second position of piston A to give minimum audibility. $\frac{1}{2}\lambda = 16.86$ cm.

disturbed conditions in the neighbourhood of the constriction, since the conductivity reaches a constant figure when the pressure-tube is about 1.9 cm. away. The intensity of the sound-waves was kept very small in an attempt to avoid vortex motion near the orifice, and reliance was placed on high amplification of the microphone output to increase the sensitivity. It was quite impossible to hear any sound from the tube by the ear alone when the tube was working.

An attempt was made to explore the shape of the wave-fronts close to the orifice by repeating the readings with the pressure-tube displaced from the axis.

The results are shown in figure 6 which shows that the wave-fronts become plane at about 1.9 cm. from the orifice, since the value of l_2 remains constant for any

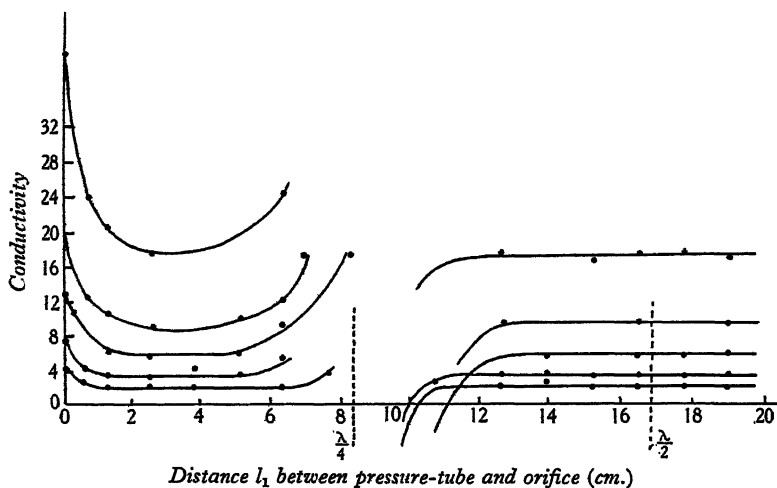


Figure 5.

displacement of the pressure-tube along a radius. The graph also shows that for a maximum displacement of the pressure-tube the variation of l_2 with l_1 is smaller

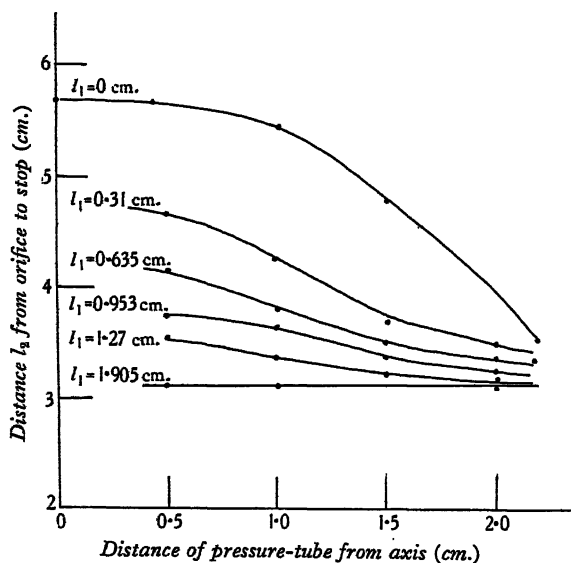


Figure 6. Graph showing the position of minimum audibility plotted against the displacement of the pressure-tube from the axis. Diameter of orifice 2.0 cm. Length 0.158 cm. $\frac{1}{2}\lambda = 16.86$ cm.

than that when the displacement is zero. It appears, therefore, that the wave-fronts become almost plane at the sides of the tube within a much less distance from the orifice than they do at the centre.

The measured conductivities have been reduced to those for an orifice in an infinitely thin plate by the following well-known relation:

$$\frac{1}{K} = \frac{1}{C} + \frac{1}{A/L} \quad \text{.....(5),}$$

where C is the conductivity in an infinitely thin plate,

A the area of the orifice, and

L the length of the orifice.

Table 2 shows this reduction from K calculated from the intercepts on figure 4. In figure 7, the ratio d/D , where d is the diameter of the orifice and D that of the tube, is plotted against C , curve (1). Curve (2) shows results obtained by Irons† by a Kundt's-tube method, assuming that the orifices referred to in his paper were 2 mm. long.

Table 2. Orifices in a tube 5.08 cm. in diameter

Diameter d of orifices (cm.)	$\frac{d}{D}$	Inter- cept from figure 4, $2\pi S/k\lambda$	K	$\frac{1}{K}$	$\frac{L}{A}$	$\frac{1}{C}$	Conductivity	
							measured	calculated from equation (6)
4.0	0.7910	0.105	35.85	0.02797	0.01254	0.0154	64.9	60.9
3.5	0.6920	0.226	16.63	0.06013	0.01642	0.04371	22.88	25.61
3.0	0.5930	0.423	9.74	0.1027	0.02240	0.08030	12.45	12.96
2.5	0.492	0.660	5.71	0.1751	0.0378	0.1373	7.28	7.16
2.0	0.395	1.09	3.45	0.2899	0.0503	0.2396	4.17	4.08
1.5	0.296	1.93	1.95	0.5128	0.0894	0.4234	2.36	2.30
1.0	0.1976	3.93	0.958	1.044	0.2012	0.8426	1.19	1.19

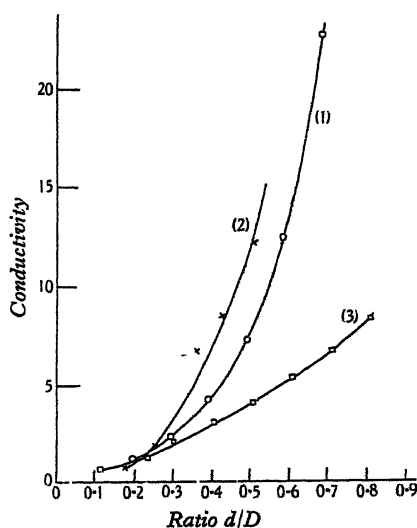


Figure 7. Curve (1), orifice forming a constriction; curve (2), Irons's results; curve (3), orifice terminating a tube.

* Cf. Rayleigh, *Sound*, 2, 181 (1896).

* *Loc. cit.*

The conductivity was assumed to depend upon the ratio of the diameters of the orifice and the tube and also on the diameter of the orifice separately, since for very small ratios of d/D the conductivity should approximate to that calculated by Rayleigh, namely d . For large orifices the conductivity should be very great and finally become infinite when $d = D$. These conditions are fulfilled by an equation of the type

$$C = \alpha d / (1 - d/D)^\beta \quad \dots\dots(6),$$

where α and β are constants.

From curve (1), figure 7, the values obtained were

$$\alpha = 0.787 \quad \text{and} \quad \beta = 1.895.$$

The last column in table 2 shows C calculated from equation (6) while the experimental values are given in the adjacent column.

The classical theory according to Rayleigh requires that $\alpha = 1$, but he assumed that the incident wave was plane and the emergent wave hemispherical. These conditions are only approximately fulfilled in the case of a constriction in a tube, as we can see by considering the velocity-potential on each side of the orifice. On the side facing the loud-speaker it is due to (i) the incident plane waves from the loud-speaker, (ii) the waves reflected from the surrounds of the orifice, and (iii) the part of the incident waves which have been transmitted through the orifice, reflected from the rigid stop, and once more transmitted through the orifice. The latter is an approximately hemispherical component. Similarly the velocity-potential on the opposite side of the orifice consists of one hemispherical and two plane components.

Orifice at the end of the tube. In order to measure the conductivities of orifices terminating a tube, the preliminary adjustments of piston B were carried out with piston A at a distance $\lambda/4$ from the pressure-tube. The main tube was then replaced by a telescopic tube with a flange on the end of the movable portion, to which the orifices were bolted. The length l_1 was varied until silence or a minimum sound was obtained in the head telephones. A baffle 5 ft. square surrounded the orifices.

§ 5. RESULTS

The results were calculated from equation (4) and are shown in table 3 for several different frequencies. The measured conductivities were reduced to what they would be in an infinitely thin plate and plotted against the ratio of the diameters of the orifice and tube; see curve (3), figure 7.

As before, it was assumed that the conductivity of the terminating orifice was given by $C = f(d, d/D)$. The end conditions are somewhat different from those in the preceding case, since when $d/D = 1$ the conductivity should be approximately twice the diameter. When d is small the conductivity should reduce to d . These conditions lead to an equation of the type

$$C = \alpha' d (1 + d/D)^\beta \quad \dots\dots(7),$$

where α' and β' are constants.

Table 3. Measured conductivities of orifices at the end of a tube at different frequencies

Diameter of orifices (cm.)	Conductivities of orifices at frequencies of				Mean K
	875	912	1000	1160 c./sec.	
4.0	6.35	6.93	7.5	7.98	7.20
3.5	5.53	5.52	5.68	6.18	5.73
3.0	4.20	4.41	4.22	4.98	4.45
2.5	3.12	3.19	3.67	3.61	3.40
2.0	2.21	2.51	2.85	2.40	2.49
1.5	1.54	1.72	1.95	1.70	1.73
1.0	0.90	1.04	1.10	1.04	1.02

From curve (3), figure 7, it was found that

$$\alpha' = 1 \quad \text{and} \quad \beta' = 1.19.$$

Table 4 shows the agreement between the measured conductivities and those calculated from equation (7). It is seen that for small orifices this equation reduces to the classical value, the conditions being exactly those assumed by Rayleigh. For large orifices, however, the equation gives higher values than those calculated theoretically. In column 6 of table 4 are tabulated the conductivities calculated from an expression proposed by A. E. Bate*, viz.

$$C = d \cdot 2^{d/D} \quad \dots\dots(8).$$

Table 4. Conductivities of orifices terminating a tube reduced to thin plate

Diameter of orifices (cm.)	$\frac{d}{D}$	K	Conductivity		
			reduced for thin plate	from equation (7)	from equation (8)
4.0	0.813	7.20	8.38	8.10	7.02
3.5	0.712	5.73	6.67	6.64	5.73
3.0	0.610	4.45	5.30	5.29	4.58
2.5	0.508	3.40	4.05	3.98	3.56
2.0	0.407	2.49	3.04	3.00	2.65
1.5	0.305	1.73	2.08	2.06	1.86
1.0	0.203	1.02	1.28	1.28	1.18

Measurements on long orifices. Measurements were made on an orifice 1.89 cm. in diameter and of length which could be increased from $\frac{1}{8}$ in. to $\frac{1}{4}$ in. in steps of $\frac{1}{8}$ in. The results are plotted on figure 8, curve (1) being the measured conductivity and curve (2) the values reduced by equation (5) to those for an infinitely thin plate. The value obtained from equation (6) is 3.59 whereas the maximum value on curve (2) is 3.11. For a long orifice forming a constriction in a tube it appears, therefore, that L in equation (5) needs to be greater than the actual length in order

* *Phil. Mag.* 10, 624 (1930).

to give an adequate correction. In this connexion it is interesting to note that G. W. Stewart*, in an experiment on the transmission ratio of a tube having a Helmholtz resonator as a side branch, had to take the conductivity of the orifice as being that of one six times the length in order to make his results agree with the theoretical transmission ratio.

Curves (3) and (4) on figure 8 show the results of measurements made on an orifice 2.5 cm. in diameter placed at the end of a tube. The lengths were increased from 0.125 to 1.91 cm. Curve (3) shows the measured conductivity while curve (4) shows the conductivities reduced to infinite thinness. In this case the "corrected" value of 3.95 agrees well with that calculated from equation (7), viz. 4.05.

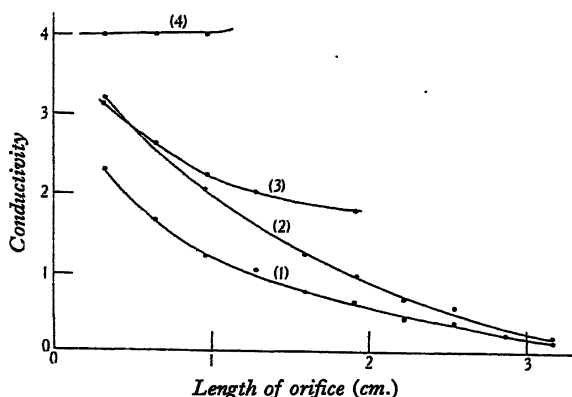


Figure 8. Effect of the length of an orifice on the conductivity. Curves (1) and (2), measured and corrected conductivities of an orifice in a tube when $\frac{1}{2}\lambda = 8.98$ cm.; curves (3) and (4), measured and corrected conductivities of an orifice at the end of a tube when $\frac{1}{2}\lambda = 18.11$ cm.

§ 6. CONCLUSION

Further experiments are being made on the conductivities of short lengths of tubes placed as constrictions and as side branches in a tube. It is also proposed to apply the method to measure the conductivity at the junction of two tubes of different areas. The method is not restricted to the measurement of conductivities, however, for it may be used equally well to measure the impedance of acoustical horns, telephone ear-caps, and microphone mouth-pieces, etc. when the resistance is small and when there are no reflected waves coming from the unknown impedance back into the tube. If there were such waves, as there would be if a Helmholtz resonator were attached at the orifice to the tube, the conductivity of the orifice would be considerably modified by the presence of the tube. Hence the measured impedance would not be that of the resonator in free space.

§ 7. ACKNOWLEDGMENTS

My thanks are due to Prof. G. P. Thomson for facilities to carry out this research and to Dr E. G. Richardson for his helpful advice and criticism.

* Stewart and Lindsay, *Acoustics*, p. 120 (1931).

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A BRIDGE FOR THE DETERMINATION OF THE FREQUENCY OF AN ALTERNATING CURRENT IN THE AUDIO-FREQUENCY RANGE

By GEOFFREY D. PEGLER, B.Sc.

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ABSTRACT. When the secondary of an air-cored transformer, of inductance N , is closed through a total resistance Q , the effective resistance P' and the effective inductance L' of the primary are given by

$$(P' - P) = p^2 M^2 Q / (Q^2 + p^2 N^2),$$

$$(L - L') = p^2 M^2 N / (Q^2 + p^2 N^2),$$

where M is the mutual inductance between primary and secondary, and p is 2π times the frequency.

If Q is varied and p is kept constant, P' becomes a maximum when $Q = pN$, and under this condition

$$(P' - P)_{\max.} = pM^2/2N,$$

which is proportional to the frequency,

while $(L - L')_{\max.} = M^2/2N = \text{a constant.}$

The above equations form the basis of the proposed method of determination of frequency, the maximum change in P corresponding to any frequency being measured by the Owen a.-c. bridge. The changes of resistance necessary to satisfy the third of the above equations may be effected with a single control, since both $(P' - P)_{\max.}$ and the corresponding value of Q are proportional to the frequency. The change required to satisfy the last equation is effected by the mere closing of a switch. The effect of residuals is discussed also.

§ 1. INTRODUCTION

THE principle of this bridge depends on the changes in effective resistance and inductance of the primary coil of an air-cored transformer as the resistance of the secondary circuit is varied. These changes may be measured with any suitable bridge, the Owen bridge being chosen because it is easily adjusted owing to the independence of its balance conditions, and because a Wagner earthing arrangement can very simply be included in it. The method dispenses with the necessity for knowing the absolute resistance of the primary coil or its variation with frequency and temperature, and gives a linear relationship between the frequency and a measured resistance.

§ 2. THEORY OF THE METHOD

If an alternating voltage be applied to the ends of the primary of two adjacent coils, then when the circuit of the secondary is closed the effective resistance of the primary rises and its inductance falls, as shown in the equations:

$$P' - P = p^2 M^2 Q / (Q^2 + p^2 N^2) \quad \dots\dots(1),$$

$$L - L' = p^2 M^2 N / (Q^2 + p^2 N^2) \quad \dots\dots(2),$$

where P and L respectively denote the resistance and inductance of the primary when the secondary circuit is open, and P' and L' their effective values when the secondary circuit is closed through a total resistance Q ; M denotes the mutual inductance between primary and secondary, N the inductance of the secondary, and $p = 2\pi f$, where f is the required frequency of the supply.

It is easily shown that, at any given frequency, P' becomes a maximum when the following condition is satisfied,

$$Q = pN \quad \dots\dots(3).$$

Under this condition equations (1) and (2) reduce to

$$(P' - P)_{\max.} = pM^2/2N = f \times \text{a constant} \quad \dots\dots(4),$$

$$(L - L')_{\max.} = M^2/2N = \text{a constant} \quad \dots\dots(5).$$

The maximum increase in P is thus simply proportional to the frequency, whilst the simultaneous decrease of L corresponding to this maximum value is independent of the frequency. These simple relations form the basis of the method of frequency-determination now proposed, and we may rewrite (4) in the form

$$\text{frequency } f = k(P' - P)_{\max.} \quad \dots\dots(4a).$$

The Owen bridge for the determination of self-inductance in terms of capacity and resistance lends itself very conveniently to the required measurement of the maximum increase in P and has accordingly been adopted.

The frequency is obtained to a close approximation by multiplying the increase in P by a constant which can be obtained initially by a simple calibration experiment at a single known frequency. The coil L , P is placed in the inductance arm of the bridge, the arrangement of which, with the symbols employed, is indicated in figure 1.

When the bridge is balanced, first with the secondary open, then with the secondary closed, the condition $Q = pN$ being attained, we have

$$L = R_1 K_3 r,$$

$$L' = R_1 K_3 r',$$

$$\text{so that} \quad (L - L')_{\max.} = M^2/2N = R_1 K_3 (r - r') = \text{a constant} \quad \dots\dots(6).$$

Thus it is seen that $(r - r')$ has always the same value, independent of the frequency.

The second condition to be satisfied in order that the bridge may be balanced is

$$R_2 = R_1 K_3 / K_4 = \text{a constant} \quad \dots\dots(7).$$

Since R_1 and K_3/K_4 remain constant at all frequencies, we may conveniently divide the arm AB into two portions, the first consisting of the primary coil and a small

variable resistance for adjusting the balance when the secondary is open, and the second consisting of a variable non-inductive resistance box S set always at the same value S_0 for the balance on open secondary. The increase $(P' - P)_{\max.}$ is then equal to the decrease $(S_0 - S)$ required to compensate this and so maintain condition (7). Thus only two balances are necessary for each frequency, one with the secondary circuit open, and the other with the secondary circuit closed and with the resistance in the arm BC diminished by the amount indicated in equation (6).

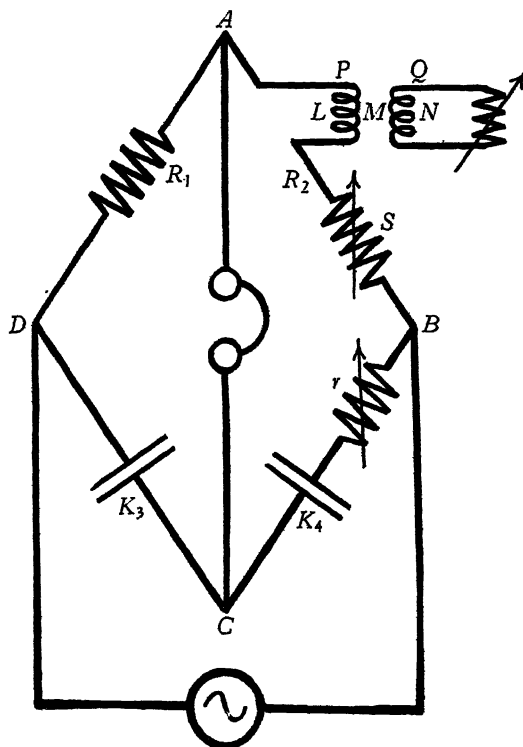


Figure 1. Theoretical circuit.

§ 3. EXPERIMENTAL PROCEDURE

To investigate the method experimentally the circuit shown in figure 2 was used, being the arrangement shown in figure 1 with a Wagner earth system added to eliminate earth-capacity effects. The resistance R_1 was a non-inductive resistance of $500\ \Omega$; K_3 and K_4 were standard mica condensers of $0.2\ \mu\text{F}$, both of the same type; and the inductances L and N were two coils of about 500 turns each, with a mean diameter of about 20 cm. S , s , and r were non-inductive resistances from boxes capable of adjustment to $0.1\ \Omega$. A fractional-ohm box reading to $0.01\ \Omega$ was also included in the arm AB . A resistance box in series with the secondary was capable of adjustment in steps of $1\ \Omega$. As a detector, high-resistance telephones were used, alone or in conjunction with a step-up transformer whose impedance matched that of the bridge.

The source of alternating current was an audio-frequency valve oscillator with a variable condenser in the grid circuit. The frequency was first set to that of one of a series of tuning-forks held near the telephone head-bands, and was maintained constant by the aid of a variable condenser of $0.0005 \mu\text{F.}$ in parallel with the main grid condenser, the capacity being adjusted until coincidence of the two frequencies, as shown by the absence of beats, was attained. The double balances at frequencies of 2048, 1024, 768, 640, 512 and 428 c./sec. were found, and the graph, figure 3, shows the observed values of $(S_0 - S)_{\text{max.}}$ plotted against frequency.

Since the ear is better able to discern the equality of two sounds of faint intensity than to find directly the point of complete silence of the fundamental in the presence

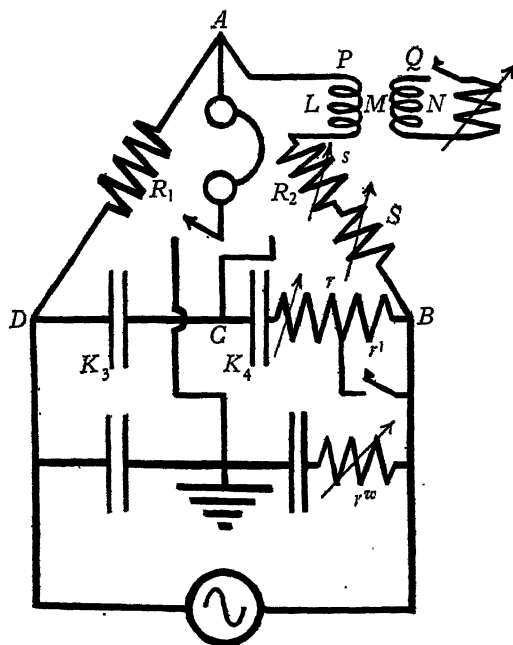


Figure 2. Experimental arrangement showing bridge with Wagner earthing arrangement.
Resistance $R_2 = P + s + S$.

of its harmonics, the procedure followed was to place in the R_2 arm a decade dial-box containing a set of $0.1\text{-}\Omega$. coils, and in series with it a $0.1\text{-}\Omega$. box subdivided to $0.01\text{ }\Omega$. The null point having been approximated to as closely as possible by a setting of the $0.01\text{-}\Omega$. dial, the $0.1\text{-}\Omega$. dial is changed alternately by $0.1\text{ }\Omega$. on either side. The correct null point is that for which the same sound-intensity occurs for each of the alternate settings. In this way accuracy to $0.01\text{ }\Omega$. in R_2 can be secured.

§ 4. CORRECTIONS DUE TO RESIDUALS

Variations from a linear relationship between $(P' - P)_{\text{max.}}$ and frequency may arise from impurity of M , and from variation of N with frequency. It has been

shown* that the phase-defect δ of induced e.m.f. in the secondary of an impure mutual inductance is given by

$$\delta = \tan^{-1} \sigma/pM,$$

where σ has the dimensions of a resistance and measures the impurity of the mutual inductance.

Thus
$$e_s = (\sigma + jpM)i_p,$$

where e_s is the induced e.m.f. in the secondary and i_p the current in the primary at the same instant.

By applying this to the fundamental formulae we can show that the effective resistance and inductance of the primary can be represented by the expressions

$$P' = P + (p^2 M^2 Q - 2p^2 M \sigma N)/(Q^2 + p^2 N^2)$$

$$L' = L - (p^2 M^2 N + 2M \sigma Q)/(Q^2 + p^2 N^2).$$

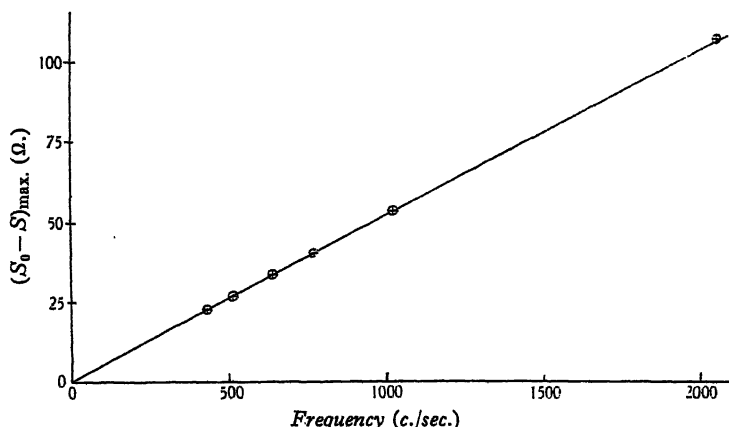


Figure 3. Variation of $(S_0 - S)_{\max}$ with frequency.

When the condition $Q = pN$ is fulfilled these equations reduce to

$$P' = P + pM^2/2N - M\sigma/N,$$

$$L' = L - M^2/2N - M\sigma/pN.$$

The effective value of P' now includes a small term independent of the frequency and the effective inductance a small term proportional to σ and inversely proportional to the frequency.

Over the audio-frequency range the change in the effective self-inductance of a coil due to change in frequency is limited to the effect of self-capacity which, in a large coil, may be quite appreciable. Regarding the distributed self-capacitance of a coil as equivalent to a small condenser of fixed value in parallel with it, we may write the vector impedance z of the coil

$$z = [R + jp \{L(1 - p^2 CL) - CR^2\}]/\{(1 - p^2 CL)^2 + p^2 C^2 R^2\}.$$

* *Proc. Phys. Soc.* 33, 312 (1921).

The effective inductance L' will be given by

$$L' \approx L/(1 - p^2 CL),$$

and the effective resistance R' by

$$R' \approx R/(1 - 2p^2 CL),$$

terms involving higher powers of C being neglected.

Since $k = N/\pi M^2$ in the expression 4 (a), a change in the value of N due to frequency may cause the observed values of $(P' - P)_{\max.}$ to depart slightly from strict linearity at high frequencies. Hence it is necessary to keep the self-capacitance of the secondary as low as possible, in which case the natural frequency of the coil will be much higher than the frequency under measurement.

§ 5. FREQUENCY-DETERMINATION

At the outset of a determination of the frequency of any source of supply the secondary is on open circuit, and the bridge is already balanced at known settings of the resistances in arms AB and BC , apart from a slight completing adjustment in the AB arm which depends on the temperature of the room. This adjustment is now made in s , and r is altered by the predetermined value r' . The secondary circuit is closed, and S and Q are now varied in conjunction until the balance is restored. The new reading of S is noted, and hence $(S_0 - S)_{\max.}$ is found. The frequency is determined to a close approximation from the relation

$$f = k (S_0 - S)_{\max.}$$

The small correction term arising from the effects discussed above is read off from a correction chart, and is added to produce the final value.

§ 6. SOME PRACTICAL CONSIDERATIONS

As is indicated in figure 3, very good correspondence with the linear law is found for frequencies up to about 1500, after which the curve rises above the straight line. This, as has been shown, is due to the variation of N with frequency, and can be reduced by making the self-inductance of the secondary coil smaller than that of the primary and by winding it in such a way as to keep the self-capacity low.

In designing an instrument embodying the method here described, the quantity $(r - r')$ could be short-circuited in the K_4 arm by means of the same switching arrangement as that which closes the secondary circuit.

Since both Q and the maximum change in S are proportional to the frequency, a single control can be provided for varying both resistances together, an auxiliary control consisting of a small rheostat being included in the arm AB to set the instrument for zero and to allow for slight changes in the resistance of the coil due to temperature fluctuations. A small rheostat can similarly be included in the arm BC to compensate for the slight variation of L with frequency.

Since k in the expression 4 (a) has the value $N/\pi M^2$, a decrease of N and an

increase of M will make the observed value of $(P' - P)_{\max}$ larger. Thus the value of M has to be made as large as possible, and this sets a limit to the reduction of N .

Figure 4 is a typical illustration of the accuracy with which the maximum setting of $(S_0 - S)$ can be approached, and shows the variation of this quantity with Q for a frequency of 768 c./sec.

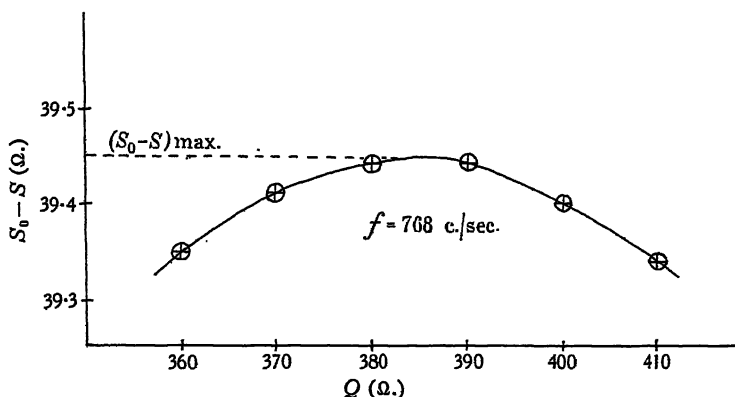


Figure 4. Variation of $(S_0 - S)$ with Q at a constant frequency of 768 c./sec.

§ 7. ACKNOWLEDGMENTS

This work was carried out in the Physics Research Laboratory of the Sir John Cass Technical Institute, London. My best thanks are due to Dr D. Owen for his advice and encouragement.

THE BAND SPECTRUM OF ARSENIC OXIDE (AsO)

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ABSTRACT. Two systems of bands have been photographed under moderately high dispersion, and their vibrational structure has been analysed. The *A* system degrades towards the red and extends from λ 3450 to λ 2950, and the *B* system degrades away from the red and extends from λ 2800 to λ 2350. Both are doublet systems, and each component band has a double head formed by two branches. The systems arise from transitions between two excited $^2\Sigma$ levels and a $^2\Pi$ ground level having a separation of 1026 cm^{-1} between the Π components.

§ 1. INTRODUCTORY

THE spectrum of arsenic oxide, so far as the author is aware, has not previously been described. His attention was directed to it by Dr R. W. B. Pearse, of the Imperial College of Science, who noted it on some plates which had been taken in a search for the spectrum of arsenic hydride. The oxide spectrum includes two systems of bands which, for convenience of reference, have been designated *A* and *B* in what follows. The *A* system consists of bands which are degraded towards the red and extend from λ 3450 to λ 2950, whilst the bands of the *B* system are degraded away from the red and occupy the region λ 2800 to λ 2350.

The vibrational analysis of the spectrum has shown that the bands originate in a diatomic molecule, and in view of the experimental conditions necessary for their production it must be concluded that the molecule is AsO. The ground level has been found to be of $^2\Pi$ type with a wide separation, and the *A* and *B* systems of bands are respectively produced by transitions from two higher levels of $^2\Sigma$ type.

§ 2. LIGHT-SOURCES EMPLOYED

The first source used to obtain the spectrum was a high-tension alternating-current arc between pieces of metallic arsenic held in suitable holders 5 mm. apart. The axis of the arc was horizontal and the current was taken from a transformer supplying about 0.2 A. at 10,000 V. Owing to the electrical instability of the arc, a stabilizing or ballast resistance was necessary. This had a maximum resistance of 25 Ω . and was connected in series with the primary winding of the transformer. The secondary current could be adjusted to a suitable value by means of this rheostat. After the arc had been running for several minutes the arsenic would catch fire, burning with a white flame and giving off clouds of oxide fumes which had to be carried into the flues by a fan. When once set alight the arsenic would,

under suitable conditions, continue to burn, and the high-tension arc thus served to brighten the flame in a manner similar to that employed in producing the spectrum of tin oxide*. The temperature of this source was comparatively low and the bands were correspondingly short, so that the weaker heads were more clearly displayed than in hotter sources.

The loose crystalline structure of the arsenic made it difficult to grip the irregular lumps satisfactorily, and also frequently caused them to fall to pieces when partly consumed in the arc. A modification was therefore introduced by which small pieces or powder could be used. The arc was arranged vertically, the lower pole being an iron cup of internal diameter 2.5 cm., holding the coarse arsenic powder, whilst the upper pole was a stout copper rod cooled by a stream of running water, figure 1. The cooling of the copper in this way prevented excessive radiation of copper lines, as a result, no doubt, of the film of arsenic compounds which condensed over the copper surface.

A discharge tube of the usual H type has also been used to obtain the AsO bands. The tube was made of pyrex with quartz windows and aluminium electrodes. A side pocket near the capillary was filled with arsenic oxide powder, As_2O_3 , and the ground stopper was fitted into place. Owing to the high temperature at which it was necessary to run the tube the ground seal could not be treated with tap grease, and a thin film of vacuum wax was melted into the groove above the stopper. After the air had been exhausted a discharge from a transformer was passed through the tube and the oxide pocket was heated sufficiently to vaporize the substance.

A third source of the spectrum was the carbon arc. The lower carbon was 18 mm. in diameter and drilled in the centre with an 8-mm. hole about 1 cm. deep. The coarse powder was packed into this cavity and the arc was struck between it and the upper 6-mm. carbon. The arc could be drawn out into a flame several centimetres long, and this was found to be the best condition for the production of the oxide spectrum. When the image of the centre of the arc was focused on the slit the B system of bands appeared in absorption. This apparently occurred as a result of absorption in the outer cool flame surrounding the white hot inner core of the arc, which emits a strong continuous radiation. This carbon-arc source was found useful in providing a simple method of obtaining the absorption spectrum, but it had definite disadvantages for the A system on account of the presence of CN bands.

The effect of temperature on the relative intensities of lines of a band has been discussed by Jevons†, and the advantages of a low-temperature source for rotational analysis has been pointed out; in the vibrational analysis also such a source is preferable to one at a high temperature. Each band is then less extensive and

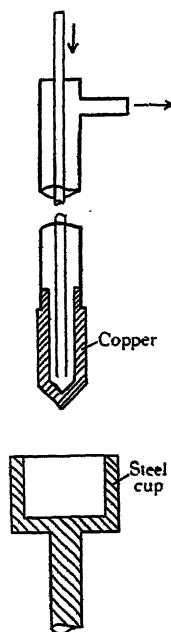


Figure 1. Water-cooled pole for high-tension arc.

* F. C. Connelly, *Proc. Phys. Soc.* 42, 28 (1933).

† W. Jevons, *Report on Spectra of Diatomic Molecules*, p. 45 (Phys. Soc. 1932).

consequently the tails of the stronger bands do not mask the weaker heads. Of the three sources described above—high-tension arc, discharge tube and carbon arc—the shortest bands were found with the discharge tube, which yields heads that appear as little more than lines. The bands in the high-tension arc also, however, are short and have been found the most suitable for measurements, whilst the self-absorption obtained in the arc has given useful confirmation of the analysis.

§ 3. DETERMINATION OF WAVE-LENGTHS

Photographs of the three sources have been obtained with Hilger quartz spectrographs E 2 and E 1; and in addition the *A* system of bands was photographed in the first order of the 10-ft. concave grating of this laboratory. The average dispersions of the three instruments in the two regions occupied by the AsO bands are as shown in table 1.

Table 1

Spectrograph	Dispersion (\AA./mm.)	
	Region <i>A</i>	Region <i>B</i>
E 2	20	9.2
E 1	6	2.8
Grating	5.4	—

Imperial Ordinary plates (H and D 150) were used, and good photographs of the high-tension arc were obtained on the E 1 spectrograph with exposures of 20 minutes. The iron arc was used as a source of reference spectra. The photographs were measured in the usual manner with a Hilger photo-measuring micrometer. The wave-lengths of the iron lines used as standards for interpolation were, as far as possible, taken from the list published by the International Astronomical Union*. These were supplemented in the region of the *B* system with vacuum-arc wave-lengths given by Burns and Walters†. Wave-lengths of all the band-heads measured are shown in tables 2 and 3, which also indicate the type of head, the v' , v'' values allotted in the analysis, the wave-numbers *in vacuo*, and the estimated intensities of the bands.

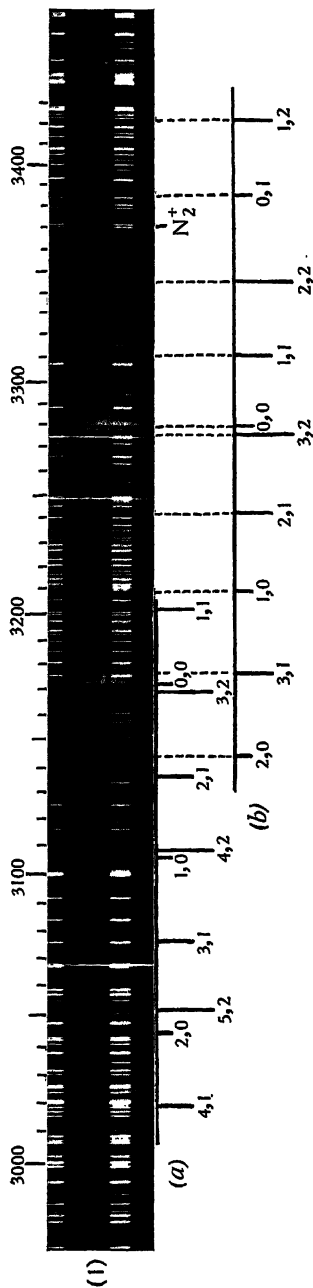
§ 4. THE *A* SYSTEM

Description of the bands. The system has a wide doublet structure in which the separation is greater than the vibrational spacing, so that its doublet character is not immediately evident. The more refrangible and the less refrangible components are indicated in the plate at (1) and in the tables and diagrams by letters (*a*) and (*b*) respectively. Thus the *a* (0, 0) is the very strong band at λ 3172.40 ($\nu = 31512.8$) and the sequences *a* (0, 0), *a* (1, 1), *a* (2, 2)—*a* (1, 0), *a* (2, 1), *a* (3, 2)—*a* (2, 0), *a* (3, 1), *a* (4, 2) form prominent features of the system. Each of these bands has itself two close heads, the separation of which varies progressively from band to band. These heads have been attributed to *R* and *Q* branches.

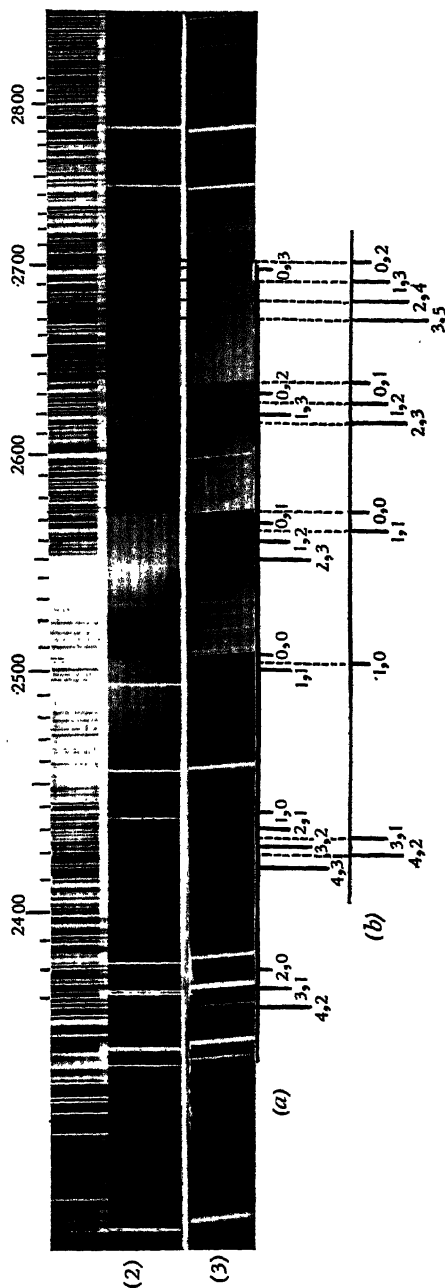
* *Trans. I.A.U.* 4, 70 (1932).

† *Publ. Allegh. Obs.* 8, No. 4 (1931).

A System



B System



- (1) The A system photographed in the high-tension arc with the Hilger E x quartz spectrograph. The close double heads of each band are due to R and Q branches. The Q heads of the principal bands are indicated by lines below the spectrum, and the doublet structure is clearly shown by the sequences of (a) and (b) components.
- (2) The B system produced in the high-tension arc and photographed with the E 2 instrument. The (a) and (b) components have been indicated as before. The vibrational spacings of the initial and final levels are nearly equal, causing close sequences, and further crowding together is due to the similarity of the doublet spacing.
- (3) The B system self-absorbed in the carbon arc. Only those bands having low values of v'' appear with appreciable strength.

Table 2. *A* system (degraded to the red)

λ in air, and intensity	ν in vacuo	ν', ν''	Type of head
3417.83 (1)	29250.0	$b(1, 2)$	Q
3415.85 (1)	29266.9	$b(1, 2)$	R
3385.22 (1)	29531.7	$b(0, 1)$	Q
3382.90 (1)	29552.0	$b(0, 1)$	R
3343.80 (1)	29897.0	$b(2, 2)$	Q
3310.71 (4)	30196.3	$b(1, 1)$	Q
3309.25 (2)	30210.6	$b(1, 1)$	R
3279.15 (9)	30486.9	$b(0, 0)$	Q
3277.21 (8)	30504.9	$b(0, 0)$	R
3275.38 (2)	30522.1	$b(3, 2)$	Q
3241.44 (4)	30841.6	$b(2, 1)$	Q
3240.11 (3)	30854.3	$b(2, 1)$	R
3209.13 (6)	31152.1	$b(1, 0)$	Q
3207.76 (4)	31165.4	$b(1, 0)$	R
3202.05 (4)	31221.0	$a(1, 1)$	Q
3200.16 (2)	31239.4	$a(1, 1)$	R
3177.60 (3)	31461.0	$b(3, 1)$	Q
3172.40 (8)	31512.8	$a(0, 0)$	Q
3170.62 (5)	31530.4	$a(0, 0)$	R
3169.13 (2)	31545.3	$a(3, 2)$	Q
3151.16 (1)	31725.2	$b(5, 2)$	Q
3150.03 (1)	31736.6	$b(5, 2)$	R
3144.14 (4)	31796.0	$b(2, 0)$	Q
3143.07 (2)	31806.8	$b(2, 0)$	R
3137.23 (4)	31866.0	$a(2, 1)$	Q
3135.59 (4)	31882.7	$a(2, 1)$	R
3123.32 (1)	32080.0	$b(4, 1)$	Q
3106.83 (6)	32177.8	$a(1, 0)$	Q
3105.64 (4)	32189.9	$a(1, 0)$	R
3075.80 (2)	32502.0	$a(3, 1)$	Q
3052.14 (1)	32754.4	$a(5, 2)$	Q
3051.50 (0)	32761.3	$a(5, 2)$	R
3045.85 (2)	32822.0	$a(2, 0)$	Q
3044.72 (1)	32834.2	$a(2, 0)$	R
3019.28 (1)	33110.8	$a(4, 1)$	Q

The (*b*) components also form well-marked sequences with spacings practically identical with those between the bands of the (*a*) sequences. Each band, however, is displaced towards the red with respect to the corresponding (*a*) component by approximately 1026 wave-numbers; e.g. the $b(0, 0)$ band is at λ 3279.15 ($\nu = 30486.9$). Again, each band has an *R* and *Q* head, the separation between them changing in magnitude from band to band in the same direction as in the corresponding (*a*) components. The system may therefore be considered to be made up of two sets of bands, the arrangement in one set being identical with that in the other but such that the bands in the first set are displaced from the second by 1026 wave-numbers.

Vibrational analysis. Table 4 shows the arrangement of the *Q* heads in a Deslandres scheme; the (*a*) and (*b*) components of each band are arranged for convenience in pairs one below the other. As the *Q* heads are very close to the origins, it may be considered that these values also represent the positions of the origins of the bands within the limits of experimental error. The next step is to derive an equation to represent all the *Q* heads by giving appropriate values to

Table 4. A system. Q heads

v' \ v''	0	1	2	$^3\Pi$
0	a { 31512.8 — b { 30486.9 955.2 Δa 665.0 Δb 665.2	{ — — 29531.7 —	—	—
1	a { 32177.8 956.8 b { 31152.1 955.8 Δa 644.0 Δb 643.9	{ 31221.0 — 30196.3 946.3 645.0 645.3	{ — — 29250.0 — 647.0	{ — — 30922.0 — 31545.3
2	a { 32822.0 956.0 b { 31796.0 954.4 Δa Δb	{ 31866.0 944.0 30841.6 945.0 636.0 620.0	{ — — 29897.0 — 623.0 625.0	{ — — 31545.3 — 30522.1
3	a b Δa Δb	{ 32502.0 947.0 31461.0 939.0 609.0 619.0	{ — — 30522.1 —	{ — — 31545.3 — 30522.1
4	a — b —	{ 33110.8 — 32080.0 —	—	—
5	a — b —	—	{ 32754.4 — 31725.2 —	—
$^3\Sigma$				

v' and v'' . In the manner indicated by W. Jevons* the following equations have been independently derived from the (a) and (b) components:

For the Q heads denoted by (a)

$$\nu = 31655.4 + [685.6 (v' + \frac{1}{2}) - 10.3 (v' + \frac{1}{2})^2] \\ - [967.8 (v'' + \frac{1}{2}) - 5.7 (v'' + \frac{1}{2})^2];$$

For the Q heads denoted by (b)

$$\nu = 30628.6 + [685.2 (v' + \frac{1}{2}) - 10.2 (v' + \frac{1}{2})^2] \\ - [966.3 (v'' + \frac{1}{2}) - 5.6 (v'' + \frac{1}{2})^2].$$

These formulae represent the observed band-heads closely, as will be seen from the values of observed and computed wave-numbers in table 5.

Table 5. Observed and computed wave-numbers

v' \ v''	0	1	2
0	a { - 0.3 b { + 0.6	{ — — + 0.5	—
1	a { + 0.7 b { + 1.0	{ - 0.7 — + 0.3	{ — — - 2.1
2	a { - 1.5 b { - 0.5	{ - 0.1 — + 0.2	{ + 0.9 — - 0.5
3	a — b —	{ + 1.2 — - 3.4	{ + 0.4 — + 1.6

* Report on Band Spectra of Diatomic Molecules, p. 60 (Phys. Soc. 1933).

The estimated relative intensities of the various bands given in the wave-lengths table are shown by the conventional method in figure 2. The values of ω_e' and ω_e'' differ considerably, so that the Franck-Condon theory would predict a relatively wide Condon parabola. It will be seen that the curve for this system bears out the general theory so far as the limited number of bands permits.

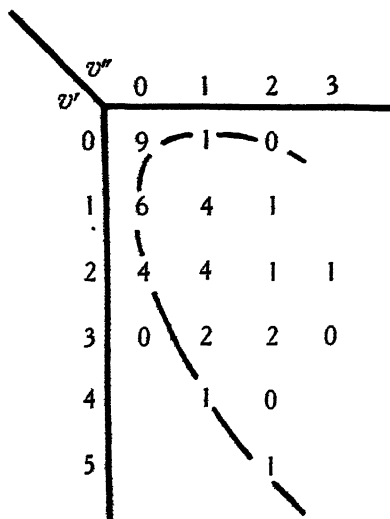


Figure 2. Relative intensities of bands in *A* system.

§ 5. THE *B* SYSTEM

Description of bands. The *B* system is illustrated in the plate at (2) and (3). It consists of five or six groups within which the bands are crowded together, with intermediate spaces almost free of bands. As in the *A* system there are close double heads, but they degrade away from the red; they are apparently *P* and *Q* heads, since the spacing varies in different bands. The confusion of the bands results from the approximate equality of three separations, namely the two vibrational spacings and the doublet spacing of the lower electronic level. This latter spacing is the same as in the *A* system (1026 wave-numbers), so that here again two components, denoted by (*a*) and (*b*), are found for each value of v' and v'' . The *a* (0, 0) and *b* (0, 0) bands are at λ 2503.64 ($\nu = 39929.8$) and λ 2570.87 ($\nu = 38903.9$) and the (*a*) and (*b*) components of each of the principal bands are indicated in the plate.

In this system also the bands may be divided into two parts: the arrangement of the (*a*) bands is the same as that of the (*b*) bands, but each of the (*a*) components is 1026 wave-numbers further from the red than the corresponding (*b*) component. The similarity is not so easy to see as in the other system owing to the overlapping, but the vibrational-analysis scheme shows the doublet nature quite definitely.

Vibrational analysis. Details of the band-heads of the *B* system are included in table 3. The *Q* heads are shown arranged in a Deslandres scheme in table 6. As before, the two components (*a*) and (*b*) are bracketed together.

Table 6. *B* system. *Q* heads

v'	v''	0	1	2	3	4	5
0	<i>a</i>	39929.8 957.7	38972.1 947.9	38024.2 934.5	37089.7	—	—
	<i>b</i>	38903.9 956.6 1086.3 1086.0	37947.3 945.2 1086.4 1085.0	37002.1 936.0 1088.0 1086.5	36066.0 1087.3 1087.0	—	—
1	<i>a</i>	41016.1 957.6	40058.5 946.3	39112.2 935.2	38177.0 921.0	37256.0	—
	<i>b</i>	39988.9 956.6 1074.8 1072.0	39032.3 943.7 1074.3 1074.0	38088.6 935.8 1073.4 1072.0	37152.8 919.0 1073.3 1065.8	36234.0 1068.0	—
2	<i>a</i>	42090.9 958.1	41132.8 947.2	40185.6 935.3	39250.3	—	37412.0
	<i>b</i>	41061.9 955.6 1061.3 1063.7	40106.3 945.0 1061.3 1063.7	39161.0 942.0 1063.0 1062.0	38218.6 916.4	37302.2 910.0	36392.0 1059.0 —
3	<i>a</i>	—	42194.1 945.5	41248.6	—	—	—
	<i>b</i>	—	41170.0 946.9 1051.0	40223.1 1051.0	—	—	37450.8
4	<i>a</i>	—	—	42299.0 942.0	—	—	—
	<i>b</i>	—	—	—	—	—	—

The formulae for the *Q* heads are derived by the method previously mentioned in connexion with the *A* system, and are as follows:

For the (*a*) components

$$\nu = 39865.7 + [1099.0 (v' + \frac{1}{2}) - 6.2 (v' + \frac{1}{2})^2] \\ - [970.0 (v'' + \frac{1}{2}) - 5.8 (v'' + \frac{1}{2})^2];$$

For the (*b*) components

$$\nu = 38839.2 + [1097.6 (v' + \frac{1}{2}) - 6.0 (v' + \frac{1}{2})^2] \\ - [968.2 (v'' + \frac{1}{2}) - 5.7 (v'' + \frac{1}{2})^2].$$

The separations between corresponding *P* and *Q* heads are shown in table 7. In spite of random variations due to errors in measurement, it will be seen that there is a definite tendency for the intervals to increase as *v'* increases and to decrease as *v''* increases. For practical purposes these intervals are the distances between *P* heads and the origins, and such changes are to be expected from the theory of the rotational structure of bands.

Table 7. *B* system. Interval (*Q* head-*P* head)

	0	1	2	3	4	5
0	<i>a</i> {16.7	{16.2	{12.1	{12.0	—	—
	<i>b</i> {18.2	{14.8	{12.1	{12.0	—	—
1	<i>a</i> {19.6	{18.5	{16.6	{14.2	{12.0	—
	<i>b</i> {17.4	{16.6	{16.5	{12.7	{12.0	—
2	<i>a</i> {21.6	{18.7	{17.6	{16.2	{11.9	{20.0
	<i>b</i> {16.4	{18.2	{17.6	{25.0	{11.9	{20.0
3	<i>a</i> —	{19.2	{19.3	—	—	{16.3
	<i>b</i> —	{19.2	{15.8	—	—	{16.3

The estimated relative intensities of the B bands are indicated by numbers in figure 3. The Condon parabola of maximum intensities is here quite narrow, and this is in agreement with the Franck-Condon principle, which predicts such a curve when the vibrational constants are nearly equal in the initial and final electronic states.

The absorption spectrum. The spectrum obtained by self-absorption of the B system in the carbon arc is shown in the plate at (3). The relative intensities of the bands completely confirm the arrangement of the vibrational scheme. Only those having low values of v'' ought to be present; in fact only the bands for which $v'' = 0$ should appear strongly, even in a vapour at a moderately high temperature. Examination of the spectrum shows in a striking manner the high intensities of

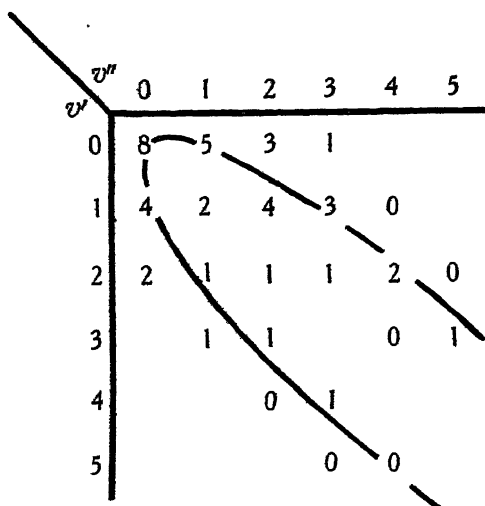


Figure 3. Relative intensities of bands in B system.

the two $(0, 0)$, $(1, 0)$ and $(2, 0)$ bands relative to the $(0, 1)$ bands which appear with relatively low intensity—compare the emission spectrum at (2)—and the $(0, 2)$ bands which are not visible at all. The appearance of the system in absorption indicates that the lower electronic level involved in the transition must be the normal or ground state of the molecule, usually denoted by X .

§ 6. CORRELATION OF THE TWO SYSTEMS

When we compare the data for the two systems, it is evident that the vibrational constants of the final levels are, within close limits, the same in both; it may therefore be concluded that the final electronic levels are equal. Furthermore, as the doublet spacing is also the same in both systems, this spacing must be that of a doublet final level. The wide spacing of this common lower level suggests a $^2\Pi$, and this is in accordance with the type assigned to the lower levels of similar systems in the spectra of NO and PO. In view of the ease with which the B system appears in absorption it may be taken that this $^2\Pi$ level is the ground state of the molecule.

The selection rules indicate that the upper levels also are expected to be of even multiplicity. The doublet spacing in the two systems is equal within the errors of measurement, so that the separations of the components of the upper levels must either be equal to each other (a very unlikely possibility) or both must be too small to be measurable. The appearance of strong Q branches shows that there must be changes in the type of level, i.e. the upper levels must be either Σ or Δ . It is very probable therefore that the levels are in each case $^2\Sigma$.

The electronic transitions concerned in the A and B systems are shown in figure 4.

The wide separation of 1026 wave-numbers between the two components of the $^2\Pi$ ground level is larger than that found in most of the molecules for which data are available. This is largely due to the fact that the spectra of very few mole-

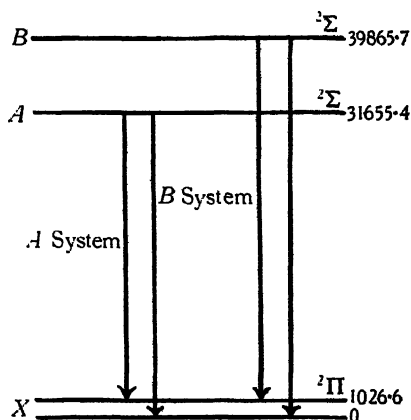


Figure 4. Electronic transitions in AsO.

cules of high molecular weight have so far been examined. SnCl^* , however, with 67 electrons has a $^2\Pi$ ground level with a spacing of 2360 wave-numbers, and HgH^\dagger with 81 electrons has 3684, whilst an excited $^2\Pi$ level of CdH^\ddagger with 49 electrons has a separation of 1000 wave-numbers. The value of 1026 in the present case is therefore in accordance with the data for molecules of similar weight, and is not excessive.

§ 7. THE ENERGY OF DISSOCIATION

Values of D , the actual energy of dissociation from the lowest vibrational energy level ($v = 0$), can be obtained by the extrapolation method of Birge and Sponer§. Numerical values for the three states of the AsO molecule have thus been calculated to be

$B (^2\Sigma)$	6.09 V.
$A (^2\Sigma)$	1.32 V.
$X (^2\Pi)$	5.68 or 4.8 V., depending on which system formula is used.

* W. Jevons, *Proc. R.S.* 110, 365 (1926).

† Hulthén, *Z. f. Phys.* 32, 32 (1925).

‡ Svensson, *Z. f. Phys.* 50, 333 (1930).

§ R. T. Birge and H. Sponer, *Phys. Rev.* 28, 259 (1926).

§ 8. RELATED SPECTRA

Of the spectra of oxides of the other elements of the fifth group of the periodic table, only that of NO has been examined at all thoroughly. In this the ground level is $^2\Pi$ and two $^2\Sigma$ and a $^2\Pi$ excited levels are known also. The separation in the ground state is 121 wave-numbers. The γ and δ bands arise from transitions between the $^2\Sigma$ states and the $^2\Pi$ ground level, and have a very distinct doublet structure, each component having close *P* and *Q* heads. Although the γ bands are actually similar to the *B* system of AsO bands, the difference in $^2\Pi$ spacing has a great effect on the appearance of the spectrum.

Two systems of bands in the PO spectrum have been described by Petrikaln* and a vibrational analysis of one of these has since been given by Ghosh and Ball†. The transition classified in this case is from a $^2\Sigma$ excited level to a $^2\Pi$ ground state having a separation of 224 wave-numbers.

The molecule NS‡ has the same number of electrons as PO, namely 23, and it is interesting to note that the separation of the $^2\Pi$ ground level is 223 cm^{-1} . There are in addition $^2\Sigma$ and $^2\Pi$ levels.

AsO with 41 electrons has, as described above, a $^2\Pi$ ground state with a separation of 1026 wave-numbers and two excited $^2\Sigma$ levels.

The remaining members of this sub-group, SbO and BiO, have been subjected to a preliminary examination, no fewer than four systems involving six levels having been proposed by Mukherji§ for SbO. The four systems are stated to be singlet ones and it appears that the vibrational constants of several of the levels are very nearly equal. Probably certain of the systems are in reality parts of a doublet system as in AsO but of even wider separation. From extrapolation, the spacing in the ground level may be expected to be of the order of 3000 wave-numbers, and such a doublet system would appear as two almost completely separated singlet ones. There is also an isotope of high relative abundance, and although the separation to be expected is rather small it may account for certain small differences in the vibrational constants of some of the levels.

A very similar arrangement of levels has been suggested for BiO by Ghosh||. Four singlet systems arising from transitions between six different electronic levels have been proposed. These also may be a doublet system similar to that suggested for SbO.

These comparisons seem to confirm the classifications which have been suggested for AsO.

§ 9. ACKNOWLEDGMENTS

The author is indebted to Prof. A. Fowler, F.R.S. for much valuable advice in the preparation of this paper, and to Dr R. W. B. Pearse for bringing the spectrum to his notice and for subsequent suggestions.

* *Z. f. Phys.* 51, 395 (1928).

† *Z. f. Phys.* 71, 362 (1931).

‡ Fowler and Bakker, *Proc. R.S.* 136, 28 (1932).

§ *Z. f. Phys.* 70, 552 (1931).

|| *Z. f. Phys.* 86, 241 (1933).

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INTENSITY MEASUREMENTS IN THE FIRST
POSITIVE BANDS OF NITROGEN

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ABSTRACT. The integrated intensities of bands in the first positive system of nitrogen have been measured by the method of photographic photometry, the high-frequency discharge, the direct-current discharge and the afterglow of active nitrogen being used as sources. The measurements show that in the cases examined the probability of transition between two vibrational levels is independent of excitation conditions.

§ 1. INTRODUCTION

IN several recent publications ^{(1), (2), (3)} it has been suggested that the probability of a transition between two energy-levels of a molecule depends upon the conditions of excitation. Further examination of this effect seemed desirable, and accordingly we have made measurements of the intensities of some of the bands of the first positive system of nitrogen. This system shows remarkable variations of intensity-distribution when different methods of excitation are used.

We have endeavoured to avoid several sources of error which may arise in photometric work of this kind.

§ 2. EXCITATION OF THE SPECTRUM

Active nitrogen. Commercial nitrogen from a cylinder was passed through a purification system consisting of tubes of phosphorus (to remove excess of oxygen), NaOH, CaCl₂ and P₂O₅. The gas was then led through a needle valve into the discharge tube, where it could be activated by a heavy condensed discharge. The resulting active nitrogen was led through a horizontal afterglow tube and was continuously pumped off as rapidly as possible by means of a Cenco Hyvac pump. The rate of the nitrogen supply was adjusted so as to give the maximum intensity of the afterglow in the horizontal tube. Light from this tube was condensed on to the slit of the spectrograph by means of a lens.

High-frequency discharge. Instead of activating the nitrogen by the condensed discharge, we fixed external electrodes to the horizontal tube and connected them to a high-frequency oscillator operating at about 10⁷ c./sec. For the high-frequency discharge the gas pressure was maintained at about 0.1 mm. of mercury.

Direct current discharge. Electrodes sealed into the horizontal tube were connected to a 1500-volt direct-current generator in series with a 30,000-ohm resistance. The current was well smoothed by means of a 1-microfarad condenser across the generator terminals, to avoid the intermittence effect of which an account is given below. The pressure of the gas in this case was about 1 mm. of mercury.

§ 3. PHOTOMETRY

The photometric procedure employed was very similar to that used in measuring the intensities of the bands of boron monoxide⁽⁴⁾. Since the active-nitrogen afterglow was very much weaker than the high-frequency or direct-current discharges the intensities of these latter were cut down with a neutral grey absorbing screen so that the same time of exposure could be used for all three modes of excitation. The exposure time for the standard lamp was also adjusted to the same value. Ilford hypersensitive panchromatic plates were found to be very suitable for the wave-length range required.

Since it was impossible to obtain with one exposure suitable densities for all the nitrogen bands, a composite absorbing screen was placed immediately in front of the spectrograph slit when these bands were being photographed. This screen consisted of three parts of different optical densities, each part covering approximately one third of the length of the slit. With this device, a single exposure gave three records of the nitrogen bands, of relative intensities about 100 : 46 : 19. The exact values of these relative intensities were determined from measurements of the peak densities of a band on each of the three spectra. With the aid of the (density, intensity) calibration curve for the plate at the appropriate wave-length the transmitted intensities were determined. It was necessary to make this determination separately for each of the three methods of excitation because of the difficulty of illuminating the length of the slit uniformly. The plate from which the final intensity-measurements were made gave the data for these determinations.

For the measurement of band-intensities, the automatic recording device described by Thompson⁽⁵⁾ was used at first, but it proved to be less satisfactory here than in the measurements of the intensities of the BO bands⁽⁴⁾. This was chiefly due to the imperfect separation of the nitrogen bands, in consequence of which there was no unexposed plate between the bands. The adjustment of the template was therefore rather difficult and uncertain.

The procedure finally adopted was to measure the densities within a band at a number of points, and to read off the corresponding intensities from the calibration curve. These intensities were then plotted against the position on the microphotometer record. For each band, the area under the resulting curve when corrected for dispersion, the energy function of the standard lamp⁽⁴⁾, and the transmission of the screen was proportional to the integrated intensity of the band. A (density, intensity) calibration curve was required for each band.

This method, though more laborious, is greatly to be preferred to the estimation of band-intensities by measurement of the peak values only, on account of possible

alterations in the intensity-distribution within a band when different modes of excitation are used.

§ 4. INTERMITTENCE EFFECT

In order to see whether the calibration curve which was obtained from exposures made with a continuous source, namely the standard lamp, could be used with the intermittent high-frequency discharge, the transmissions of the composite screen were measured by means of exposures made with these two sources. When corrections were made for a slight lack of uniformity in the illumination over the length of the spectrograph slit the results agreed to within 3 per cent. From this we infer that the intermittence effect is not appreciable with the high-frequency discharge. The effect of the discharge from the d.-c. generator was quite different, however, unless the discharge was smoothed. Examination with a cathode-ray oscillograph showed that the generator voltage was subject to large periodic fluctuations, and this apparently resulted in a lack of agreement between the screen transmissions measured when the standard lamp and the discharge tube respectively were used as sources. The difference was of the order of 7 per cent. When the generator voltage was smoothed, this difference disappeared.

§ 5. RESULTS

The final results of the measurements are given in the table. All the bands in the red, yellow and green sequences which were of sufficient intensity have been measured, with the exception of the 4-1 band at $\lambda = 6788 \text{ \AA}$. At this point the

Table. Intensities of bands in the first positive system of nitrogen

Band	Measured intensity			Intensity \times correlation-factor	
	Active nitrogen	Direct-current discharge	High-frequency discharge	Active nitrogen	Direct-current discharge
5-1	—	38.6	16.8	—	15.8
5-2	—	40.2	15.4	—	16.4
6-2	—	76.5	33.3	—	31.6
6-3	—	45.3	17.7	—	18.7
7-3	—	62.3	36.7	—	36.3
7-4	—	20.9	12.0	—	12.2
8-4	—	58.2	30.0	—	31.2
8-5	—	11.8	6.6	—	63.3
9-4	—	9.2	5.02	—	4.90
9-5	—	57.1	30.0	—	31.0
9-6	—	74.0	39.1	—	39.5
10-5	—	10.4	4.61	—	4.87
10-6	12.8	62.0	29.4	30.6	29.1
10-7	9.9	52.1	24.5	23.7	24.4
11-6	10.2	12.6	6.80	6.24	6.85
11-7	52.0	55.3	30.0	31.8	30.1
11-8	27.0	28.9	15.9	16.5	15.7
12-7	5.90	9.15	7.45	7.50	7.14
12-8	19.0	32.7	24.4	24.1	25.5
12-9	5.55	20.9	15.1	7.1	16.3
4-0					

change in plate sensitivity with wave-length becomes too rapid to allow of accurate intensity-measurements.

The intensities in the second, third and fourth columns differ on account of differing population of the upper levels, but it seems likely that the probability of transition between levels should be independent of excitation conditions. If this is true, the intensities of any band when excited by the three different methods should be proportional to the populations of the upper states in the three cases, and the proportionality factors should be constant for all bands having a common upper vibrational level.

This seems to be the case. The mean values of these factors have been found for each upper level, and by means of these the intensities of bands in the direct-current discharge and in the afterglow have been adjusted to the values which they would have had if the population of the upper levels had been the same as the population of these levels in the high-frequency discharge. The fifth and sixth columns of the table give the results of this adjustment, and it will be noticed that the agreement with the values in the fourth column is in most cases very close. The only marked deviation occurs in the 12-9 band, but this can be explained by the superposition of the 4-0 band, which is of appreciable intensity in the high-frequency and direct-current discharges, but is very weak in the afterglow⁽⁶⁾.

On the basis of the whole of the results it may be concluded that the transition-probabilities in the three modes of excitation agree to within about 3 per cent, the maximum individual deviation being 7 per cent. We attribute these small deviations to experimental error, due chiefly to imperfect separation of the bands.

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ON THE AUTOMATIC REGISTRATION OF THE AMPLITUDE OF DOWNCOMING WIRELESS WAVES

PART I

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ABSTRACT. An adaptation of the Breit and Tuve method of echo delineation, by means of which it is possible to obtain a continuous record of the amplitude of the wireless waves reflected from the ionized regions of the earth's atmosphere, is described. An optical system is used to separate the records made on the photographic paper by the first and second reflections. Attention is directed to the different types of signal fluctuations that may occur. Examples of an interference phenomenon between the two magneto-ionic components of the downcoming waves are described. The reflection coefficient of the ionized regions is discussed and a rapid method of finding the relationship between this coefficient and the frequency of the waves is described.

§ 1. INTRODUCTION

SOME observations on the amplitude of wireless waves refracted by the ionized regions of the earth's atmosphere have been described in a previous paper⁽¹⁾. The majority of the results given in that paper were obtained by using the Breit and Tuve method of echo delineation, in conjunction with a cathode-ray oscillograph, in the well-known manner. The relative amplitudes of the refracted waves were measured by means of snapshot photographs of the trace on the screen of the oscillograph, these photographs being taken about once every minute. By this method it was possible to work out the general characteristics of the diurnal variation in amplitude of the downcoming waves. The method failed, however, to record the very rapid changes in amplitude that are known to occur, and it is obvious that, for a more complete study of the amplitude-variations, some form of continuous record is desirable. It is only from such a record that it is possible to find out the cause of these rapid variations. In this paper a simple modification of the Breit and Tuve method is described by means of which a continuous record of the amplitude of the downcoming waves may be obtained.

A method of recording which gives the amplitude as well as the equivalent height of reflection of the waves has been described by Hollmann and Kreielsen⁽²⁾. It is desirable for many reasons to know the equivalent height of reflection of the waves whose amplitude is being recorded, and in the method described below this is achieved by means of a second oscillograph on a separate record. Although this is an extra complication it is considered to add to the efficiency of the method.

The picture traced out on the screen of the cathode-ray tube when the Breit and Tuve method is being used is well known. In its simplest form it is similar to figure 1 (a), in which G represents the signal that has travelled to the receiver over the ground path while F_1 and F_2 are the echoes once and twice reflected from the upper region. The more complex cases that are commonly met with are shown in figures 1 (b), 1 (c) and 1 (d), which represent respectively single and double reflection from region E , a single reflection from region E together with single and double reflections from region F , and finally magneto-ionic splitting of the first

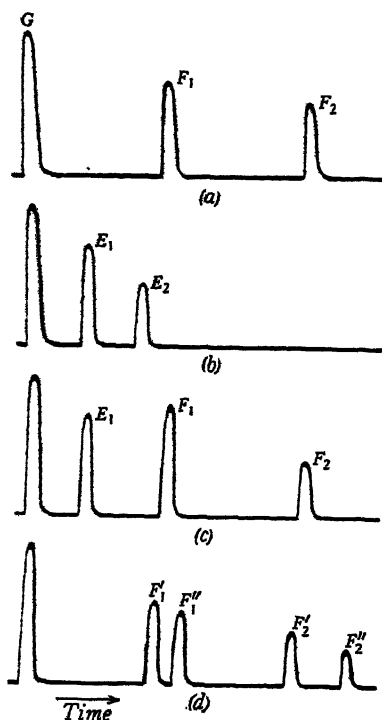


Figure 1.

and second reflections from region F . With the simple echo pattern shown in figures 1 (a) and 1 (b) continuous recording of the amplitude of each component is relatively simple, but with the more complex forms it is more difficult to obtain a record that will give a clear account of the behaviour of each component.

§ 2. EXPERIMENTAL METHOD AND APPARATUS

For the simpler cases that have been mentioned above one naturally turns to a direct method of recording which is similar in some respects to that of Hollmann and Kreielsheimer. The trace on the screen of the cathode-ray oscillograph is arranged so that the time base is vertical while the displacements due to the ground ray and the echo are horizontal, as shown in figure 2 (a). An image of this trace is

formed by a camera lens on a strip of photographic paper which is made to travel vertically upwards, as shown in figure 2 (b). The picture obtained is much improved by the use of two screens, one of which will allow only the top of the ground ray to appear, while the other prevents the time base from forming too dark an impression. Only a small section of the time base is exposed to the paper. As the amplitude of the first reflection varies it forms a trace of varying distance from the base line on the photographic paper, while the second reflection doubly exposes

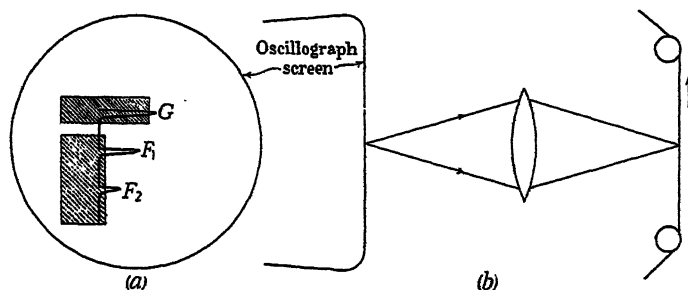


Figure 2.

the paper and leaves a darker trace. An example of a record obtained with this method is shown in figure 3. This simple method of recording has been found to be very satisfactory for comparing the amplitude of the first reflection with that of the ground ray under simple conditions. It does not, however, give a very good trace of the second reflection, for this tends to become mixed up with the first reflection, especially when each of these components is varying considerably in

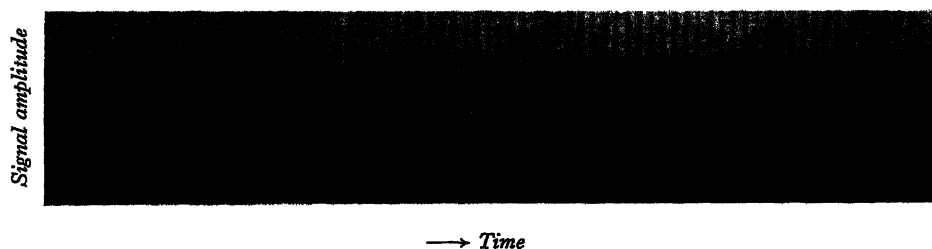


Figure 3. Comparison of ground ray and first reflection from region F.

amplitude. Since it is hoped that the most important results of this work will be the measurement of the total absorption suffered by the waves, to be effected by means of a comparison of the amplitudes of the first and second reflections, the method so far described was considered to be unsatisfactory and the following modification was introduced.

In order that a record of the amplitude of the first and of the second reflections may be obtained on different parts of the photographic paper, an optical system consisting of eight prisms was introduced between the camera and the screen of the cathode-ray oscillograph. The trace on the screen of the oscillograph was arranged with the time base vertical as in the above example. Four exactly similar

right-angled prisms are mounted as shown in figure 4 so that the image of the portion of the time base covered by prism A is displaced towards the right to a distance equal to half the width of one of the prisms. Vertically and immediately below this set of prisms is another similar set of four, arranged so that while the prism A' is directly beneath A , the two prisms B' and C' are displaced through half the width of a prism towards the left, and D' is displaced a whole width in this direction. With this arrangement the optical distance from all parts of the screen covered by A and A' to the camera lens is the same, while the top and bottom parts of the time base appear, when viewed from the camera, to be displaced to the right and left respectively. The vertical thickness of the prisms and the total length of the time base are fixed so that, for example, the first reflection may fall behind the prism A while the second reflection is behind A' . The thickness of the prisms,

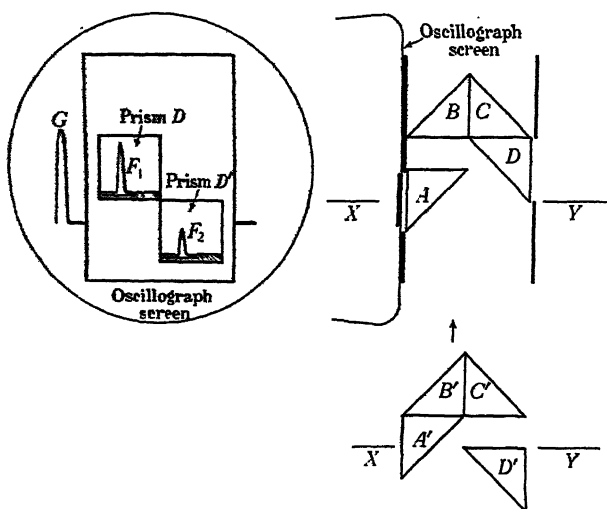


Figure 4.

corresponding to a distance measured along the time base, is sufficient to allow a considerable change in the equivalent height of reflection of the waves, without the component considered moving out of the range covered by A or A' .

The arrangement of the camera is, as before, with the paper moving vertically upwards. The alignment of the camera and the prisms is carried out by focusing the image of the time base on a ground-glass screen which replaces the photographic paper for this purpose. Opaque screens are used to eliminate excessive darkening of the paper by the time base.

By the use of an adjustable magnetic deflection of the cathode-ray beam the whole pattern on the screen of the oscillograph may be moved vertically upwards or downwards so that the positions of the reflected components may be adjusted with respect to the prisms A and A' . This adjustment may also be used for selecting the components to be recorded. For instance, when no second reflection is being received the pattern may be moved downwards so that the first reflection and the

ground wave may be compared, or it may be adjusted so that reflections from region *E* are recorded. Examples of records obtained with this apparatus are shown in figures 5 to 10.

§ 3. DISCUSSION OF RESULTS

In the experiments that have been carried out with this apparatus the pulse signals were transmitted from the roof of the East Wing, King's College, London, and were received at the Halley Stewart Laboratory only six and a half kilometres away. In all cases, therefore, the waves are incident at practically normal incidence on the refracting regions of the upper atmosphere. At the receiving station reception was carried out on a superheterodyne receiver, for which the output, measured as a deflection on the screen of the oscillograph, was linearly related to the signal amplitude. It is of very great assistance in the elucidation of the records obtained with this apparatus, to receive the signals on some form of aerial which will discriminate between the two magneto-ionic components of the downcoming waves. It is well known that theoretically each of these components should be returned from the refracting regions circularly polarized, one component having a right-handed sense of rotation (the extraordinary ray) and the other a left-handed sense (the ordinary ray). A number of records have been obtained with a circularly polarized aerial of the type described by J. A. Ratcliffe and E. L. C. White⁽³⁾. It may be mentioned that it has been found that usually the magneto-ionic components are not exactly circularly polarized but are elliptically polarized, the ratio of the axes being commonly of the order of 10 : 9.

Experiments with the apparatus have not been continued for a long enough period to enable an exhaustive study of the phenomena connected with the efficiency of reflection by the ionized regions to be made. There are, however, several features of the work which may be conveniently discussed to illustrate the method of recording. The results described below have been obtained with signal frequencies from 3 to 4 Mc./sec. The most obvious feature of the records is that they show up remarkably well the rapid variations of the amplitude of the reflected waves; it may be said that the amplitude of the reflected waves is rarely steady for more than a few seconds. At times the variation in amplitude is fairly slow, giving only two or three maxima per minute, but much more often it varies very rapidly. It is possible to recognize two distinct types of fading, type (*a*) being of a very regular nature which is associated with the interference of the two magneto-ionic components, and type (*b*) usually of a more irregular nature which occurs when only one of the magneto-ionic components is being received. Examples of type (*a*) can be seen in figures 5 and 7 while type (*b*) is exhibited in figure 8. It will be noticed that this method of recording has a distinct advantage over other methods for investigating fading by means of continuous-wave signals since interference effects can take place only between two downcoming components which have suffered approximately the same group-time delay. It is this time delay which determines whether two components will energize the receiving aerial practically simultaneously and so interfere, whereas it is the optical path difference which determines their relative phase angle.

Fading of type (a) is very satisfactorily accounted for as a phenomenon of interference between the extraordinary ray and the ordinary ray when there is a temporal change in the optical path difference for these two components, while the equivalent path difference between them is insufficient to cause them to be separated along the time base. Consider the example shown in figure 5. This record was obtained on

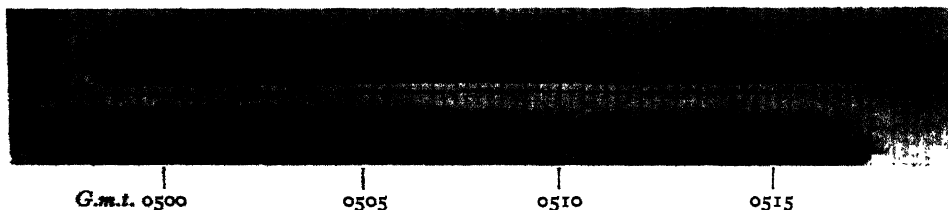


Figure 5. May 8, 1934. First and second reflection from region *F*.

the morning of May 8, 1934. Figure 6 shows the equivalent height measurements for May 8. Reflection of the extraordinary ray from region *F* had persisted throughout the night, while the ordinary ray had penetrated that region early in the previous evening. At 0435 G.m.t. it was once more returned from region *F*, its equivalent

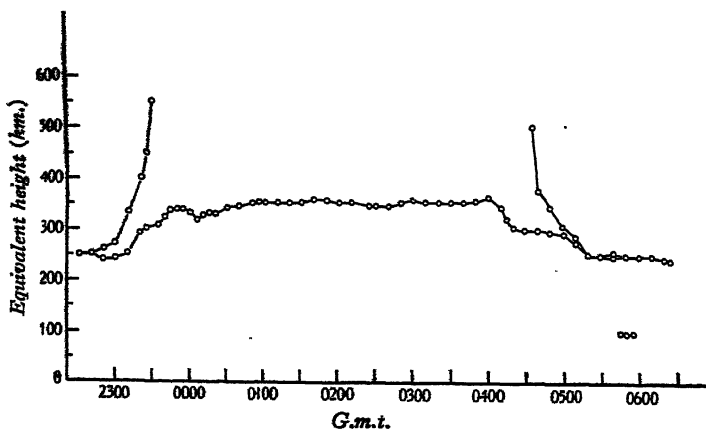


Figure 6. May 8, 1934. $f=3.4$ Mc./sec.

height of reflection being, to begin with, 500 km., while the equivalent height for the extraordinary ray was only 300 km. Within 20 minutes, however, the equivalent height for the former ray had fallen to almost exactly 300 km., so that the two components coalesced in the cathode-ray pattern. This can be seen very clearly on the record of equivalent heights which was taken at the same time as the amplitude record. If it be remembered that the equivalent-height record is not capable of revealing quite small differences in height between the two components, then it seems certain that although these two components (*F* ordinary and *F* extraordinary) are returned from almost exactly the same equivalent height; there is

still a small optical path difference between them which is changing with time so that the resultant intensity fades periodically as the waves go in and out of phase.

In figure 7 is shown another example taken at a slightly later time, 0530 G.m.t. The equivalent height record shows clearly that the extraordinary and ordinary rays tended to separate slightly from one another at this time, while the amplitude record shows the fading that resulted. As the optical path difference of the ordinary ray increases the amplitude varies in a periodic manner until, after about 7 minutes, these components are sufficiently resolved for each to leave its own trace.



Figure 7. May 8, 1934. Ground ray and first reflection, region F.

With the known speed of movement of the photographic paper, time marks being made on the record every half hour, it is possible to calculate the number of maxima per minute and from this the rate of change of the optical path difference, $d(\delta P)/dt$, between the two components. These measurements are given in table 1 for the two examples quoted above, it being assumed that a change from one maximum to the next signifies a change in the optical path difference of one wave-length.

Table 1. Rate of change of optical path difference. Wave-length 88 m.

Time (G.m.t.)	Number of maxima per minute	$\frac{d}{dt}(\delta P)$ (km./min.)
0500	6.0	0.53
0507	10.0	0.88
0513	6.0	0.53
0517	1.5	0.13
0529	3.0	0.26
0532	5.5	0.48

It will be noticed, in the first example given above, that while the first reflection exhibits very regular maxima and minima the second reflection does not do so. There are two reasons which may be advanced to explain this. It will be remembered that the difference in group-time delay for the two components of the doublet after the second reflection is twice that for the first reflection. Thus, while the first two echoes may overlap sufficiently to produce interference, the second two may not do so. Then the reflection coefficient for the ordinary ray may be very different from that of the extraordinary ray, so that although the first reflections of both rays

may be of comparable amplitude, the second reflection of one of them may be quite small. An examination of the records shows that both these causes are effective in preventing interference between the two components after second reflection.

Fading of type (b) is differentiated from type (a) chiefly by the fact that it occurs when only one of the two magneto-ionic components is being received. In such a case it is usually found that the fluctuations in amplitude are more irregular than those of type (a), but this is not necessarily so. During the night of May 7-8 for instance the extraordinary ray only was reflected from the *F* region and its amplitude variations could be very easily studied. In the early part of the night the variations were slow, but as the night advanced they became more rapid and irregular. There were several occasions on which very regular variations occurred. The records shown in figure 8 illustrate the fading that took place from 2340 to 0010 G.m.t. and from 0050 to 0120 G.m.t. A period of regular fading can be seen

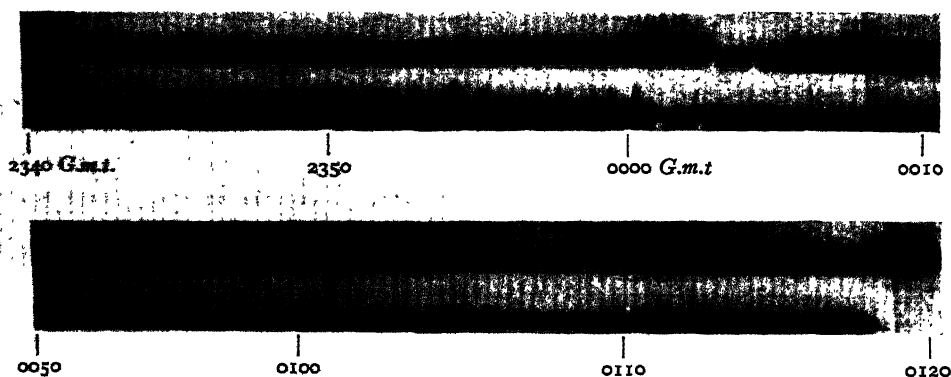


Figure 8. Extraordinary ray, region *F*.

about 0120 G.m.t. In the same figure from 2346 to 0000 G.m.t. there is an example of a period when the amplitude of the second reflection was on occasions greater than that of the first reflection. There seems to be no definite relationship between the amplitude-variations of the first and second reflections.

The results during this period are analogous to those obtained by Appleton and Ratcliffe⁽⁴⁾ in 1927 using waves of frequency about 0.75 Mc./sec. In their case the ordinary ray only from region *E* was observed during the night, the extraordinary ray being absent owing to absorption. From their observations it was concluded that "The changes in the downcoming wave are real intensity changes (as measured at the ground) and are not due to the rotation of a plane-polarized wave." Also "Although the cause of signal-variations has been traced mainly to intensity-fluctuations of the downcoming rays as measured at the ground we must not regard these fluctuations as being due to the alterations in the reflecting-power of a fixed flat surface, for other observations seem to indicate that these intensity-fluctuations are themselves the result of an interference mechanism the nature of which is at present somewhat obscure."

In the light of the present work something can be added to the conclusions of Appleton and Ratcliffe. Firstly, with the higher frequencies and for reflection from region *F*, when the extraordinary ray only is received during the night, or when the ordinary ray only is received during the day, the fluctuations in amplitude are similar to those found by Appleton and Ratcliffe with the lower frequencies and for reflection from region *E*. It is known that in the present investigation the fluctuations in amplitude frequently observed with the circularly polarized aerial, under either of the above conditions, show that the downcoming waves are always very nearly circularly polarized. The view that the changes in amplitude are caused by an interference mechanism is very strongly upheld by such an example as is shown in figure 8, where the maxima and minima are very similar to those found when interference between the two magneto-ionic components is known to be taking place. Although it is not yet certain how this interference mechanism operates, the variations in amplitude can be more satisfactorily accounted for in this way than by an assumption of very rapid variations in the total absorption suffered by the waves.

§ 4. BURSTS OF INTENSITY

Another interesting phenomenon which has been noticed on several occasions is one which may be called "bursts of intensity." It occurs during the daylight hours and has been observed with signal-frequencies of from 3 to 4 Mc./sec. During the daylight hours the ordinary ray only is normally received with frequencies of this order, the amplitude of the extraordinary ray being very small as a result of absorption. It is found that, while the amplitude of the ordinary ray may be for the most part quite small, sudden increases occur at fairly regular intervals in the

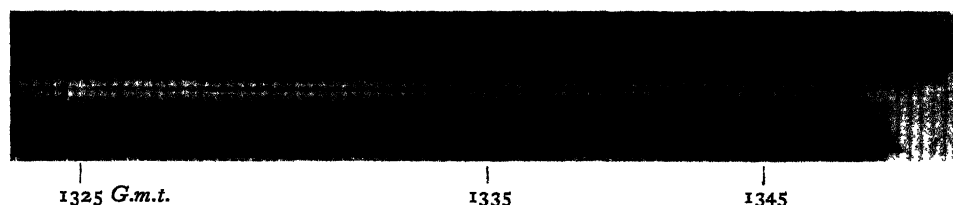


Figure 9. March 28, 1934. Ground ray and first reflection, region *F*.

intensity of this component. Most of the observations relate to the amplitude of the first reflection, but on one occasion, when the intensity of the first reflection was very great, the same phenomenon was found to occur in the case of the second reflection. A typical example of the phenomenon is shown in figure 9. This record, which was taken on March 28, 1934, from 1325 to 1345 G.m.t., shows the ground ray and the first reflection from region *F*. During most of the time the amplitude of the first reflection is small, but it increases at intervals of about 12 minutes to a very much greater value. This maximum usually lasts for about 3 minutes and is fairly steady throughout that period. On several other occasions the same phenomenon has been observed, and it is found that the length of the interval between

bursts is usually of the same order. In table 2 are given data showing the regularity with which the bursts occur.

Table 2. Interval (minutes) between bursts of intensity

February 20, 1934 3.6 Mc./sec.	March 28, 1934 4 Mc./sec.		April 6, 1934 4 Mc./sec.
15	10	11	12.0
19	15	19	8.5
15	13	12	5.5
—	8	11	7.0
—	14	—	—
Average 16 minutes	Average 12.5 minutes		Average 8.6 minutes

Although perhaps seen to better advantage on the amplitude records, these bursts of intensity are of course evident on the (equivalent-height, time) records (P' , t). On these records they show up as short periods during which second and even third reflections are obtained at times when only the first reflection is normally obtained. It would seem therefore that what actually happens is that the average intensity of each reflection is increased. It may be concluded therefore that for very short periods during the daylight hours the reflecting region, which is on the average a poor reflector, becomes a much better one.

§ 5. THE REFLECTION COEFFICIENT

It has been pointed out by Appleton and Ratcliffe⁽⁵⁾ that if the radiating characteristics of the transmitting aerial are known, so that the relative amplitudes of the waves sent upwards to the ionized regions and of the ground wave can be found, then the decrease in the amplitude of the atmospheric wave due either to electron-limitation or to absorption can be expressed in terms of a reflection coefficient. This coefficient ρ was defined as

$$\rho = \alpha \frac{F}{G} \cdot \frac{d_1}{d_0},$$

where α is a constant depending on the transmitting aerial and upon the attenuation suffered by the ground wave, F and G are, respectively, the amplitudes of the downcoming wave from region F and the ground wave, and d_1 and d_0 are the distances travelled by these waves. The chief difficulty in the measurement of ρ by comparing F and G lies in the determination of α . This difficulty is immediately removed if it is possible to compare the amplitudes of the first reflection and the second reflection. Consider a wave that has suffered a single reflection at region F . This wave will be returned to the ground with an amplitude F_1 . After reflection at the ground it will be reflected by the F region for the second time and returned to the ground with amplitude F_2 . As has been shown above, the fact that these two echoes return to the receiver with different group-time delays makes it possible to measure the amplitude of each separately. In the case of vertical incidence the amplitude F_1 of the first reflection may be equated to $\beta\rho/d_1$, where β is a constant,

whereas the amplitude F_2 of the second reflection will be $\beta\rho^2\rho_1/2d_1$. It may be assumed that the coefficient of the layer for the second reflection is the same as that for the first reflection, while the spherical waves will have travelled twice the distance d_1 . In this expression ρ_1 is the reflection coefficient for the ground.

Thus from a measurement of F_1 and F_2 the ratio F_2/F_1 or $\rho\rho_1/2$ may be obtained. Since it is reasonable to assume that the coefficient for the ground is very nearly unity the value of ρ may be calculated directly from the equation

$$\rho = 2F_2/F_1.$$

A further extension of this reasoning is immediately possible. The amplitude G of the ground wave at the receiver will be related to the distance travelled by the equation

$$G = \delta/d_0.$$

Thus

$$\frac{F_1}{G} = \frac{\beta}{\delta} \cdot \frac{d_0}{d_1} \cdot \rho,$$

while

$$F_2/F_1 = \rho/2.$$

If therefore G , F_1 and F_2 are simultaneously observed, the constant

$$F_1^2/2F_2G \text{ or } (\beta/\delta) \cdot (d_0/d_1)$$

may be obtained. If this constant is observed at a time when it is possible to measure G , F_1 and F_2 , then, with the same settings of the transmitter and receiver, ρ can be obtained at other times when only G and F_1 are obtainable, due allowance being made for any alteration in the distance travelled by the waves. In practice observations on either the ordinary or the extraordinary ray can be made, so that the reflection coefficient for either component can be obtained.

From what has been said above it is obvious that the average values of F_1 and F_2 must be used in calculating the reflection coefficient. In table 3 there are given values of this coefficient for the extraordinary ray during the night of May 7/8. It will be seen that in some cases the coefficient is greater than unity, a fact which supports the hypothesis that the variations in amplitude are due to rays scattered from irregularities in the refracting regions⁽⁶⁾.

Table 3. Reflection coefficient, May 7/8, 1934

Time (G.m.t.)	ρ	Time (G.m.t.)	ρ
2340	0.75	0206	0.60
2350	2.00	0220	1.42
0000	1.60	0240	0.40
0010	0.50	0255	0.43
0052	1.20	0300	0.30
0120	1.00	0320	0.25

§ 6. RELATIONSHIP BETWEEN THE REFLECTION COEFFICIENT AND FREQUENCY

It has been amply demonstrated by Appleton that a vast amount of information about the ionized regions of the atmosphere can be obtained from an experimental determination of the relationship between the equivalent height P' of reflection of the waves and the frequency f . It will readily be appreciated that the study of the fading of the downcoming waves and of the general diminution in intensity due to absorption or electron-limitation might be aided by a similar line of attack. With this in mind the present method of recording has been used to determine what might be called the "reflection-coefficient, frequency" relationship. The ideal result would be obtained from a rapid determination of the reflection coefficient for a number of different frequencies following one another in rapid succession. Owing to the constant fading of the echoes, however, the amplitude must be re-

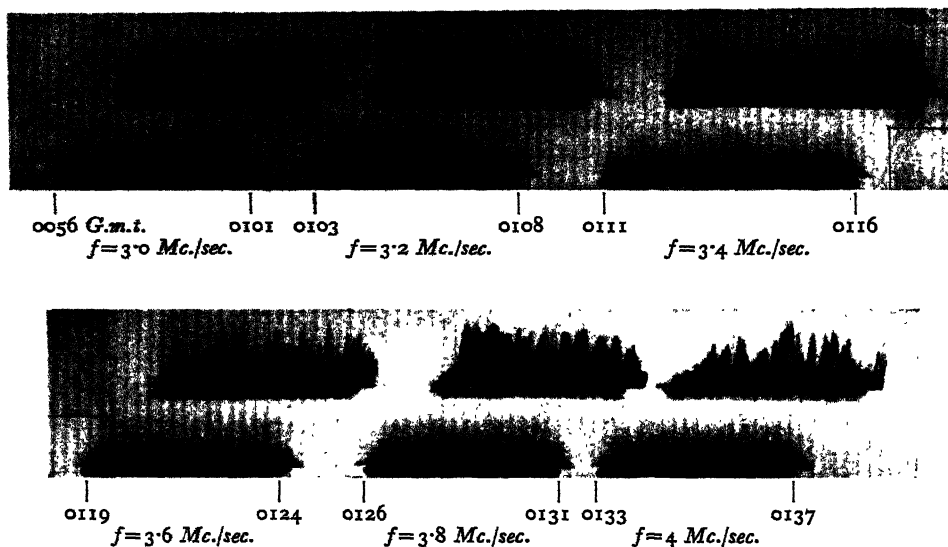


Figure 10. First reflection and second reflection, region F .

corded for sufficient time to allow a fair sampling of the average value for each frequency to be obtained. On the other hand it is desirable to cover the whole range of frequency in as short a time as is reasonably possible, in order to eliminate the possibility of major alterations in the atmospheric ionized regions. An examination of the fading records described above indicates that a good average value of the amplitude could be obtained in 5 minutes.

In figure 10 is shown a series of records of the amplitude of the first and second reflections from region F obtained during the night of May 14, 1934. The frequencies progress in steps of 0.2 Mc./sec. from 3 to 4 Mc./sec. These results were obtained with an ordinary inverted- L aerial. From the P', f curve which was taken simultaneously with this record it can be seen that both the extraordinary and the

ordinary rays were present, with the same group-time delay, so that the amplitude recorded is the resultant of these two components. Measurements of the average values of the amplitudes of the first and second reflections show that the ratio F_1/F_2 is very nearly constant over this relatively small range of frequency. The average value for the ratio is 0.3. These results serve to illustrate the facility with which amplitudes may be compared for a number of different frequencies.

§ 7. ACKNOWLEDGMENT

I wish to express my thanks to Prof. E. V. Appleton for his encouragement and interest in this work. The work described in this paper was carried out as part of the programme of the Radio Research Board of the Department of Scientific and Industrial Research.

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A BALANCE-DETECTOR FOR ALTERNATING-CURRENT BRIDGES

By C. R. COSENS, M.A.

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ABSTRACT. A balanced valve arrangement with a portable d.-c. galvanometer of pointer type is described for use as balance-detector in a.-c. bridge work. Over an extensive range of frequencies its sensitivity is comparable to that of a vibration galvanometer or telephone. The direction of deflection shows which way the bridge must be adjusted to secure a balance as in the case of a d.-c. bridge or electro-dynamometer, but the false-zero effect found with the latter is absent. The arrangement could be adapted for use at radio frequencies.

§ 1. INTRODUCTION

A PERUSAL of Hague's *A.-C. Bridge methods*, in which descriptions and references are given for a large number of devices which are or have been used as balance-detectors, reveals that in this country at least the vibration galvanometer for low frequencies and the telephone for higher frequencies are in almost universal use, with a few instruments of dynamometer type. When increased sensitivity is required valve amplification may be used, but when the addition of an amplifier is once admitted we can use other devices which without such aid would be too insensitive. Experiments on rectifiers of various types led to the construction of a device, having certain advantages, which is herein described.

§ 2. COMPARISON OF KNOWN DEVICES

The vibration galvanometer is unsurpassed for use at a single fixed frequency if this is comparatively low, say < 250 c./sec. When measurements have to be made over even a small range of frequencies, retuning for each frequency takes time, whereas if a frequency-range of more than, say, 3 or 4 to 1 is wanted, it is usually necessary to change the coil and suspension, and while this operation may be easier on some makes of instrument than on others, it is an inconvenience with any instrument.

The telephone is insensitive at low frequencies, and the ear at very high ones, and in any case a silent room is desirable unless amplifiers are used with a loud-speaker. Furthermore, a visual indication is to be preferred to an aural one for accurate work.

An electro-dynamometer, such as Sumpner's, has many advantages. It can be used throughout a long frequency-range without adjustment, and gives an indication of the sense of the change needed in the bridge to secure balance. These advantages are counterbalanced by the grave disadvantage that a false zero is obtained when

the electro-dynamometer is used on bridges of low impedance, owing to electromotive forces which are induced in the moving coil by the transformer action of the main field.

§ 3. SOME ELEMENTARY VALVE DEVICES

Many valve devices of well-known types can be used satisfactorily. For instance a valve amplifier may be followed by a Moullin voltmeter, or another rectifier, such as a crystal detector or Westinghouse rectifier. All suffer from the fact that for a small applied e.m.f. they necessarily operate as square-law devices, and although they can be made sufficiently sensitive by using amplifiers of high gain there is always the difficulty that any large error in balance is likely to damage the galvanometer unless unremitting attention is given to the necessity for shunting this instrument heavily until balance is nearly reached.

Alternatively a Sumpner electro-dynamometer, with the moving coil connected in the anode circuit of a high-impedance valve (triode, screen-grid tetrode, or pentode) is sensitive and satisfactory, the false zero effect being almost completely eliminated; but similar results can be attained without using a reflecting instrument.

§ 4. VALVE-DYNAMOMETER PRINCIPLE

If a thermionic valve draws its anode supply not from a d.-c. battery but from an alternating source at the same frequency as that supplying the bridge, it will pass a certain rectified direct current which can be measured on a d.-c. galvanometer; this current will vary with the potential of the grid. If an alternating potential be applied to the grid from the detector branch points of the bridge, this rectified current will be increased or reduced, according as the grid potential is cophased or antiphased to the anode potential; and *the magnitude of this change is proportional to the first power, not the square, of the grid potential.*

In order to obtain sensitivity, it is desirable that the steady deflection of the d.-c. galvanometer should be balanced out by any well-known method, but there is then difficulty from wandering zero with change of supply voltage, a difficulty which can be overcome by using a second similar valve as a balancing-device, by which means we also obtain a doubling of the sensitivity.

Several devices of this nature were experimented with, and the circuit shown in outline in figure 1* was finally adopted as the most satisfactory.

§ 5. VALVE GALVANOMETER FOR ALTERNATING CURRENT

The author's device in its final form is shown diagrammatically in figure 1, the filament batteries and grid-bias arrangements being omitted for the sake of simplicity. Deferring consideration of the thin-line (grid) circuits, and confining attention to the thick lines, we may note a resemblance to the full-wave rectifier employed extensively for the high-tension supply of wireless receivers.

The primary of the transformer T_1 is supplied with alternating current of the same frequency as that used in the measurements on the bridge, and the two secondaries supply antiphased voltages to the anodes of valves V_1 and V_2 . During

* British patent specification no. 385,982 (January, 1933).

one half-cycle current will flow in the valve, say V_1 , whose anode is positive with respect to its filaments, returning via R_1 and causing a fall of potential from c to a ; similarly, during the other half-cycle V_2 will pass current which returns via R_2 from c to b . If the two valves were identical these currents when averaged over a complete cycle would be equal, and a and b would be at the same mean potential. If the valves are not exactly similar, an adjustment of R_2 will secure the necessary equality of potential. Let this be referred to as the *no-signal state*, the signal being the e.m.f. across the detector branch points of the bridge. In this state a d.-c. galvanometer G connected between a and b will carry no current, when the current is averaged over a complete cycle. To prevent pointer-wobble at low frequencies due to alternating current in the galvanometer, the choke-condenser arrangement Ch, C , in figure 1 is adopted.

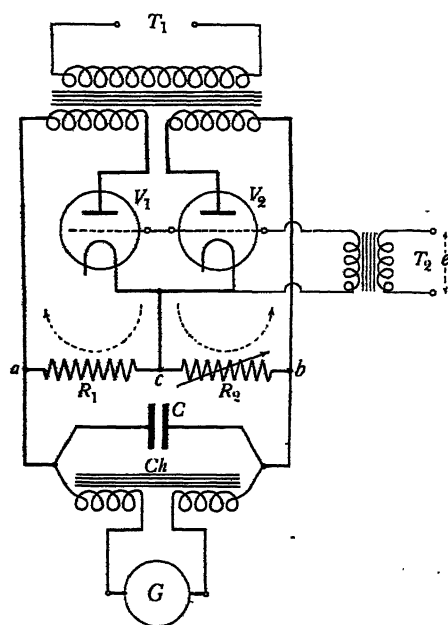


Figure 1.

If now the terminals of the grid transformer T_2 be connected to the branch points of the bridge, across which we suppose a potential-difference e to exist, a deflection of the galvanometer G will in general result. Suppose first that the phase of e is such that the grid and anode of V_1 reach their maximum positive values simultaneously. Then during the half-cycle in which the anode of V_1 is positive its grid also is positive, and it passes a larger anode current than in the no-signal state. The anode of V_2 being negative no current flows in V_2 . During the next half-cycle the anode of V_1 is negative and this valve is therefore inoperative, but the anode of V_2 is now positive and it passes a current; but since the grid of V_2 is now negative, it passes less current than it did in the no-signal state. The effect of the potential e is therefore to cause V_1 to pass more current, and V_2 to pass less,

than in the no-signal state, and this difference of currents causes a difference in the potential-drops ca and cb , so that a and b are no longer at the same mean d.-c. potential and a current flows in the galvanometer G . It is easily seen that a reversal of e will reverse the galvanometer deflection.

It is shown in the Appendix that if e is not in phase with the anode voltage of one of the valves, but lags behind it by an angle ϕ , the galvanometer current is approximately proportional to $e \cos \phi$.

§ 6. FREQUENCY-SELECTIVITY

The device is frequency-selective; though not absolutely free from deflection by e.m.f. of frequencies other than that supplied to T_1 , owing to inexact matching of valves etc., the frequency-selectivity is ample for most purposes. It is interesting to note that it is possible to make the device sensitive to all frequencies except a specified frequency, to which it does not respond. For this purpose the grids are supplied as shown in the figure, but both anodes are supplied from one half of the secondary of T_2 , being connected together. If the valves were exactly similar the effect of e applied to the grids would be to affect both valves equally, and no difference of anode currents would exist to deflect G . This might be useful in certain cases, e.g. for the indication of nerve-response, the nerve being stimulated by alternating current, and the anodes of the valves being supplied at the stimulation frequency. The device would be sensitive to the nerve response, which would not be at exactly stimulation frequency, but the effects of leakage of stimulation current would be very much reduced.

§ 7. PHASE-SELECTIVITY

Like all instruments having the characteristics of a dynamometer, i.e. in which the instantaneous deflecting torque on the indicator is dependent on the product of

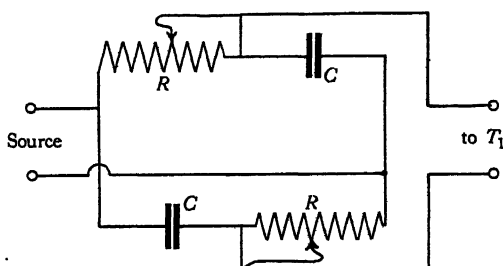


Figure 2. (Resistances R are ganged.)

two quantities and not on the square of a single quantity, the device is phase-selective; that is to say that it indicates the component of e in phase with the main supply to the valve anodes via T_1 . Thus if T_1 be connected across the a.-c. source which supplies the bridge the device will be sensitive to errors of resistance-adjustment but not of reactance-adjustment; to obtain sensitivity to errors of reactance-adjustment a phase-shift of approximately $\pi/2$ must be introduced. Any well-known phase-shifting device may be used, such as a phase-shifting transformer or

a resistance-capacity combination; one of the best of these, described in *The Cathode-Ray Oscillograph in Radio Research* by Watson-Watt, Herd, and Bainbridge-Bell, is shown in figure 2, in which the two capacities C are equal and the two resistances R are ganged so as to be always equal to one another. Provided that the load on this phase-shifter is of impedance high compared to that of the C, R combination, there is little change of magnitude in the output p.d. and a phase-shift of about 120° is readily obtainable.

The phase-shifter may be introduced between the source and the input terminals of T_1 , or between the detector branch points of the bridge and the input terminals of T_2 , or between the output terminals of T_2 and the valve-grids, the last-mentioned arrangement being perhaps the best.

The balancing of the a.-c. bridge is then simplified, the procedure being as follows. With zero phase-shift, the resistance of the bridge is adjusted until balance is indicated. A phase-shift of about $\pi/2$ is then introduced, and the reactance is adjusted. These two operations are repeated until balance is obtained in both for the same setting of resistance and reactance. The ability to adjust resistance and reactance separately enables the final adjustment to be reached with great rapidity.

§ 8. FREQUENCY LIMITS AND SENSITIVITY

The device can be used at almost any frequency if suitable components are employed. If T_1, T_2 are transformers of the type used in commercial audio-frequency amplifiers, the frequency limits are those at which the transformers cease to operate efficiently. If specially designed transformers are used there seems to be no reason why the method could not be adapted for use at radio-frequencies.

Owing to the balancing out of the mean anode currents (of the order of say 2 mA.) of the valves, the balance is not much affected by voltage changes, and G may be a centre-zero unipivot galvanometer giving full-scale deflection for 12 microamperes, suitable shunts being used for the preliminary adjustments. The ratio of the sensitivity of the twin-valve arrangement described to that of an unbalanced arrangement would then be as 12 μ A. is to 2 mA., or 1000 : 6, even if the e.m.f. e were applied to the grid of only one valve, the grid of the other being maintained at constant potential. But as the two valves operate differentially on the galvanometer G , which in effect measures the difference of their anode currents, the sensitivity is doubled and becomes 2000 : 6, or say 300 times as great as with an unbalanced arrangement. For this it is necessary to have a fine adjustment of the balancing resistance R_2 ; and experiment shows that if an attempt is made to balance a similar circuit with one valve replaced by a resistance, the balance is rapidly upset by small changes of supply voltage. However, with the two-valve arrangement described the device is to a large extent self-compensating for this sort of variation.

In the completed instrument sensitivity is almost independent of frequency, and is comparable with that of a vibration galvanometer at 50 c./sec. and with that of a telephone at 500 c./sec.

§ 9. COMMERCIAL FORM OF INSTRUMENT

While the arrangement shown in figure 1 can be set up temporarily and made to work, with the component parts widely spread over the laboratory table, certain difficulties arise when the whole is assembled in a metal screening-box of reasonable size. These difficulties have now been overcome and several refinements have been added, such as a fine adjustment to the rheostat R_2 , balanced and screened transformers for T_1 and T_2 , with primary tapplings to suit a source and bridge of varying impedances, a self-contained unipivot galvanometer with suitable shunts to reduce the sensitivity during preliminary adjustments, and a properly filtered automatic grid-bias.

The instrument is now made in a commercial form by the Cambridge Instrument Co. Ltd.

APPENDIX

APPROXIMATE MATHEMATICAL ANALYSIS

Let $\mu = [\partial v_a / \partial v_g]_{i_a}$ and $\rho = [\partial v_a / \partial i_a]_{v_g}$ for each valve and let $R_1 = R_2 = R$.

Let i , v_a , v_g be the instantaneous anode current, anode potential and grid potential, respectively.

Assume that

$$i = \frac{1}{R + \rho} (v_a + \mu v_g) \quad [v_a > 0]; \quad i = 0 \quad [v_a < 0].$$

For valve V_1 , let $v_a = V \sin \omega t$; $v_g = E \sin (\omega t + \phi)$.

$$\text{Then } i_1 = \frac{1}{R + \rho} (V \sin \omega t + \mu E \sin [\omega t + \phi]) \quad [0 < \omega t < \pi],$$

$$i_1 = 0 \quad \dots\dots\dots [\pi < \omega t < 2\pi].$$

Writing I_1 for the mean value of i over a cycle, and putting $\theta = \omega t$ we have

$$I_1 = \frac{1}{2\pi} \left[\frac{1}{R + \rho} \int_0^\pi [V + \mu E \cos \phi] \sin \theta \, d\theta + \int_0^\pi [\mu E \sin \phi] \cos \theta \, d\theta + \int_\pi^{2\pi} (0) \, d\theta \right],$$

$$I_1 = \frac{1}{\pi [R + \rho]} [V + \mu E \cos \phi].$$

Similarly for the mean anode current of V_2 we have

$$I_2 = \frac{1}{\pi [R + \rho]} [-V + \mu E \cos \phi].$$

$$\text{Therefore} \quad I_1 - I_2 = \frac{2}{\pi [R + \rho]} \mu E \cos \phi.$$

Now $(I_1 - I_2)$ must flow from b to a , i.e. through the galvanometer of resistance g , shunted by $2R$. Hence the galvanometer current

$$\begin{aligned} &= \frac{2R}{g + 2R} (I_1 - I_2) \\ &= \left[\frac{2R}{g + 2R} \frac{1}{R + \rho} \frac{2\mu}{\pi} \right] E \cos \phi. \end{aligned}$$

SPECIAL CASES OF THE MUTUAL INDUCTANCE BETWEEN CIRCLES, WITH SOME PRACTICAL APPLICATIONS*

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Communicated by Dr H. R. Nettleton, April 26, 1934.

ABSTRACT. This paper contains the results of some practical work on the mutual inductance between coils. It shows that equations relating to the ideal case of circles can be applied to multi-layered coils under conditions giving (a) constancy of the mutual inductance between twin coils connected in conjunction and a smaller coil sliding on a rod through the centre of symmetry O of the pair, for certain distances between the twin coils and certain angles made by the rod with their planes; (b) proportionality between mutual inductance and displacement for the same coils if the twin coils are connected in opposition; (c) proportionality between mutual inductance and angle if a large central coil is rotated about a diameter through the centre of symmetry O of the twin coils, for certain conditions as to the distances between the twin coils and the ratios borne by the radius of the central coil to that of either of the twin coils; and (d) proportionality between mutual inductance and the sine of the angle between the twin coils and a solenoid rotating symmetrically between them, for given dimensions of the solenoid.

The paper also gives a simple method for determining the absolute magnetic moment of a magnet, in which the need for corrections for the dimensions of the magnet is avoided.

§ 1. THEORY

CONSIDER two coaxial circles A and B , each of radius a , separated one from the other by a distance $2x$, figure 1. O is their centre of symmetry through which passes a line MN making an angle θ with the planes of the circles. With its centre along this line, at a distance l from O , is another circle C of smaller radius α lying in a plane perpendicular to MN . The distances of O from the periphery of A (or B) and C are r and s respectively, while ψ and ϕ are the angles subtended by the radii of A and C respectively at O . The mutual inductance M_J between A and B in conjunction (i.e. with their magnetic fields in the same direction) and C is given by

$$M_J = Gq \sum_{n=1}^{\infty} \frac{2}{n(n+1)} \left(\frac{s}{r}\right)^{n-1} P_n'(\cos \psi) P_n'(\cos \phi) P_n(\sin \theta) \dots (1),$$

where $q = \pi a^2$ and is the area of the small circle C ; $G = t \cdot 2\pi a^2 / r^3$ and is the galvanometer constant of A and B in conjunction at the origin O ; t is the total number of turns on A and B together, if these are considered as coils with the turns

* Part of a thesis accepted for the degree of Doctor of Philosophy, by the University of London.

of each coincident; P_n is the Legendre function of the first kind of order n , P_n' its first differential coefficient and n is an odd positive integer*.

For M_p , the mutual inductance between A and B in opposition and C , equation (1) holds except that n is now an even positive integer. G , however, is still the galvanometer constant of A and B in conjunction. In practical work it is easier to deal with the relationship in terms of the radii and separation of the circles than in

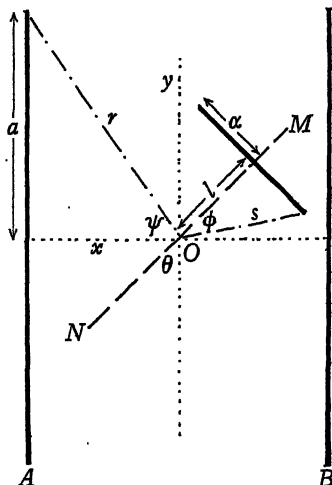


Figure 1.

terms of functions of the angles they subtend, so it is convenient to expand equation (1) in terms of x , a , l and α as follows:

$$\begin{aligned}
M_J/Gq &= \frac{1.2}{2} \sin \theta \\
&+ \frac{3.4}{2} \cdot \frac{1}{r^4} \left[x^2 - \frac{a^2}{4} \right] \left[l^2 - \frac{\alpha^2}{4} \right] P_2(\sin \theta) \\
&+ \frac{5.6}{2} \cdot \frac{1}{r^8} \left[x^4 - \frac{3}{2} x^2 a^2 + \frac{a^4}{8} \right] \left[l^4 - \frac{3}{2} l^2 \alpha^2 + \frac{\alpha^4}{8} \right] P_4(\sin \theta) \\
&+ \frac{7.8}{2} \cdot \frac{1}{r^{12}} \left[x^6 - \frac{15}{4} x^4 a^2 + \frac{15}{8} x^2 a^4 - \frac{5}{64} a^6 \right] [F_7(l, \alpha)] P_7(\sin \theta) \\
&+ \dots\dots\dots \\
&+ \frac{n(n+1)}{2} [F_n(x, a)] [F_n(l, \alpha)] [1/r^{2(n-1)}] P_n(\sin \theta) \dots\dots(2),
\end{aligned}$$

where n is odd and $F_n(x, a) = \frac{2}{n(n+1)} r^{n-1} P_n'(\cos \psi) \dots\dots(2a),$

and
$$F_n(l, \alpha) = \frac{2}{n(n+1)} s^{n-1} P'_n(\cos \phi) \dots (2b).$$

* *Proc. Phys. Soc.* **44**, 198 (1932).

The first few terms of M_P/Gq are as follows:

$$\begin{aligned} M_P/Gq &= \frac{2 \cdot 3}{2} \cdot \frac{1}{r^2} x l P_2(\sin \theta) \\ &+ \frac{4 \cdot 5}{2} \cdot \frac{1}{r^6} \left[x \left(x^2 - \frac{3}{4} a^2 \right) \right] \left[l \left(l^2 - \frac{3}{4} \alpha^2 \right) \right] P_4(\sin \theta) \\ &+ \frac{6 \cdot 7}{2} \cdot \frac{1}{r^{10}} \left[x \left(x^4 - \frac{5}{2} x^2 a^2 + \frac{5}{8} a^4 \right) \right] [F_6(l, \alpha)] P_6(\sin \theta) \\ &+ \frac{8 \cdot 9}{2} \cdot \frac{1}{r^{14}} \left[x \left(x^6 - \frac{21}{4} x^4 a^2 + \frac{35}{8} x^2 a^4 - \frac{35}{64} a^6 \right) \right] [F_8(l, \alpha)] P_8(\sin \theta) \\ &+ \dots\dots\dots (3). \end{aligned}$$

The direct evaluation of $F_n(x, a)$ or the corresponding $F_n(l, \alpha)$ is laborious if n is large, but it can be shown by a theorem of spherical harmonics that if n is odd

$$F_{n+1}(x, a) = n \int_0^x F_n(x, a) dx \quad \dots\dots(4),$$

and if n is even

$$F_{n+1}(x, a) = n \int_0^x F_n(x, a) dx + (-\frac{1}{2})^{n/2} a^n \frac{1 \cdot 3 \cdot 5 \dots (n-1)}{[(n+2)/2]!} \quad \dots\dots(5),$$

whence each term can be obtained from its preceding term.

Lines of isomutual inductance, A and B in conjunction. Examination of equation (2) shows that if x^2/a^2 is made equal to $\frac{1}{4}$ —the well-known Helmholtz criterion—its second term vanishes. If we now choose θ so that $P_5(\sin \theta)$ is zero ($\theta = 64^\circ 59'$ or $32^\circ 35'$) then the third term also disappears and any variation from constancy of $M_J/Gq \sin \theta$ depends on the fourth and succeeding terms. We can, however, make the second and third terms of equation (2) vanish in another way. The distance between A and B can be chosen so that $x^4 - \frac{3}{2}x^2a^2 + a^4/8$ is zero ($x^2/a^2 = 0.08856$ or 1.41144 , the former being the useful solution) and θ can be chosen so that $P_8(\sin \theta) = 0$ ($\theta = 50^\circ 46'$). Once again departure from constancy of $M_J/Gq \sin \theta$ depends on the fourth and following terms. In either of these arrangements it can be shown by substituting the appropriate values of θ and x that further terms are negligible. Practical work described later bears out this conclusion.

Lines of constant inductance-gradient, A and B in opposition. In a similar way if in equation (3) we make the conditions such that $x^4 - \frac{5}{2}x^2a^2 + \frac{5}{8}a^4 = 0$ and $P_4(\sin \theta) = 0$, then M_P/Gq is proportional to l . The useful value of x^2/a^2 , viz. 0.281754 , taken with $\theta = 19^\circ 53'$ or $\theta = 59^\circ 27'$ gives us conditions under which equal shifts of C along MN , figure 1, give equal changes in the mutual inductance between A and B in opposition and C . As before, terms after the third can be shown to be negligible.

Effect of multiplicity of layers. In the above discussion A and B have been taken as single-turn circles, or as coils all of whose turns are coincident. Such coils cannot be constructed in practice, but by treating the problem as in a previous

paper* we can find the correcting factors f_1, f_2, f_3 , for the first three terms of equation (2) due to the presence of multiple layers. If $2b$ is the axial breadth and $2d$ the radial depth of A or B ,

$$f_1 = 1 - \frac{1}{2} \cdot \frac{b^2}{a^2} \cdot \frac{a^4}{r^4} \left(1 - 4 \frac{x^2}{a^2} \right) + \frac{1}{3} \cdot \frac{d^2}{a^2} \cdot \frac{a^4}{r^4} \left(1 - \frac{11}{2} \cdot \frac{x^2}{a^2} + \frac{x^4}{a^4} \right) \dots\dots(6),$$

$$f_2 = 1 - \frac{5}{2} \cdot \frac{b^2}{a^2} \cdot \frac{a^4}{r^4} \left(1 - 12 \frac{x^2}{a^2} + 8 \frac{x^4}{a^4} \right) / \left(1 - 4 \frac{x^2}{a^2} \right) + 2 \frac{d^2}{a^2} \cdot \frac{a^4}{r^4} \left(1 - \frac{53}{4} \cdot \frac{x^2}{a^2} + \frac{34}{3} \cdot \frac{x^4}{a^4} - \frac{2}{3} \cdot \frac{x^6}{a^6} \right) / \left(1 - 4 \frac{x^2}{a^2} \right) \dots\dots(7),$$

$$f_3 = 1 - \frac{35}{6} \cdot \frac{b^2}{a^2} \cdot \frac{a^4}{r^4} \left[1 - 24 \frac{x^2}{a^2} + 48 \frac{x^4}{a^4} - \frac{64}{5} \cdot \frac{x^6}{a^6} \right] / \left[1 - 12 \frac{x^2}{a^2} + 8 \frac{x^4}{a^4} \right] + 5 \frac{d^2}{a^2} \cdot \frac{a^4}{r^4} \left[1 - \frac{151}{6} \cdot \frac{x^2}{a^2} + 55 \frac{x^4}{a^4} - \frac{92}{5} \cdot \frac{x^6}{a^6} + \frac{8}{15} \cdot \frac{x^8}{a^8} \right] / \left[1 - 12 \frac{x^2}{a^2} + 8 \frac{x^4}{a^4} \right] \dots\dots(8).$$

The correcting factor f_1 for the fundamental term has not the importance in this investigation that it has in absolute galvanometry since the corrected fundamental term is measured experimentally. Now either f_2 or f_3 can be made to be unity (and so the second or third terms can be made independent of multiplicity of layers) if b/d is made 0.928 or 0.957 when $x^2/a^2 = 0.25$ or 0.08856 respectively. For practical purposes, if the twin coils are constructed with a square cross-section, whose side is small compared with the mean radius of the windings, the effect of multiplicity of layers is negligible. Now for each position of constant mutual inductance one term is made independent of multiplicity of layers by the shape of the windings of A and B and so can be made to vanish for the value of x/a appropriate to a coil whose turns are coincident while the other term, which vanishes by choice of θ , vanishes whether A and B possess multiple layers or not. Hence lines of isomutual inductance can be obtained even when the main coils are multi-layered.

The mutual inductance between twin coils A and B and a solenoid S . If the coil C is replaced by a solenoid S lying symmetrically with its axis on MN , it is easy to show by the integration of the effect of all its elements that the mutual inductance M_θ between twin coils A and B and S is given by

$$M_\theta/GQ = \frac{1.2}{2} \sin \theta + \frac{3.4}{2} \cdot \frac{1}{r^4} \left[x^2 - \frac{a^2}{4} \right] \left[\frac{L^2}{3} - \frac{\alpha^2}{4} \right] P_3(\sin \theta) + \frac{5.6}{2} \cdot \frac{1}{r^8} \left[x^4 - \frac{3}{2} x^2 a^2 + \frac{a^4}{8} \right] \left[\frac{L^4}{5} - \frac{L^2 \alpha^2}{2} + \frac{\alpha^2}{8} \right] P_5(\sin \theta) + \dots\dots\dots + \frac{n(n+1)}{2} \cdot \frac{1}{r^{2(n-1)}} \left[\frac{2}{n(n+1)} r^{n-1} P_n'(\cos \psi) \right] \times \left[\frac{2}{n(n+1)(n+2)} s_1^{n-1} \frac{P_{n+1}'(\cos \phi_1)}{\cos \phi_1} \right] P_n(\sin \theta) \dots\dots(9),$$

* *Proc. Phys. Soc.* 44, 201 (1932).

where $2L$ is the length of the solenoid, s_1 is the distance from O to the periphery of the outside turn, ϕ_1 is the angle subtended by the radius of the outside turn at O , and Q is the total area of the solenoid.

Design of a solenoid to measure θ . It is possible, for all values of x/a and θ , to make the second term of equation (9) vanish by making $L^2/3$ equal to $\alpha^2/4$. If α is small with respect to a , then the importance of the third and successive terms is small and hence, for a solenoid constructed so that its total length is $\sqrt{3}$ times its radius and arranged to lie symmetrically with its axis on MN , the mutual inductance M_θ between it and A and B in conjunction is proportional to $\sin \theta$, and M_θ/M_{90} gives $\sin \theta$, where M_{90} is the value of M_θ when $\theta = 90^\circ$. Such a solenoid can conveniently be called an angle solenoid. Its use in measuring angles will be justified practically later.

The measurement of the absolute moment of a magnet. If a magnet of moment m lying along MN with its centre at O replaces S , then the flux F threading A and B is given to a high order of accuracy by

$$F = mG \sin \theta \quad \text{.....(10),}$$

when its magnetic axis lies along a line of isomutual inductance*.

If S also lies at this angle

$$M_\theta = GQ \sin \theta \quad \text{.....(11).}$$

If now the mutual inductance between S and a standard solenoid of constant G_s is M_s , then $Q = M_s/G_s$, and combining these expressions we find that

$$m = \frac{F}{M_\theta} \left(\frac{M_s}{G_s} \right) \quad \text{.....(12).}$$

The correcting factor f_1 for non-coincidence of turns, being involved in both (10) and (11), has been eliminated and equation (12) gives the absolute moment of a magnet directly in terms of a flux, a ratio of two mutual inductances and a solenoid constant.

§ 2. EXPERIMENTS ON THE MUTUAL INDUCTANCE BETWEEN TWIN COILS IN CONJUNCTION AND A SMALL COIL

The apparatus. This was arranged as in figure 1. Practical details are shown in figure 2. The coils A and B were wound on formers of dexionite. The coil channels were square in cross-section, in accordance with the conditions laid down in § 1 for the correction of the effect of multiplicity of layers. The radial depth and axial breadth were 3.6 cm. Each coil had 504 turns of double-silk-covered copper wire (s.w.g. 16) of mean diameter 32.8₂ cm. The coil C used in this section was of axial length 0.8 cm. It consisted of 1100 turns of double-silk-covered copper wire (s.w.g. 38). As its total area q was 2290 cm², its average diameter was 1.62₈ cm. The coil was arranged to slide axially on a wooden rod held in a circular ebonite framework so that, when the framework was rotated on its spindles EE , the rod always passed through the centre of symmetry O , of A and B . The displacement of C along the rod was measured by a scale marked on the rod. The angle θ made by the rod with

* See also *Proc. Phys. Soc.* 42, 506 (1930).

the planes of *A* and *B* could be estimated by means of a pointer *F*, but was accurately determined by the ratio of the mutual inductances between *A* and *B* in conjunction and *C* at zero displacement, first at the given angle and then when θ was 90° . Since *C* was small this ratio gave $\sin \theta$. A check coil wound on the circular ebonite framework was used to find out if θ had been altered accidentally during a series of readings for the same angle. The check was easily performed by measuring the mutual inductance between this coil and *A* and *B* in conjunction, at intervals during the readings.

Method. *A* and *B* were set co-axially and symmetrically about the axis *EE* of the circular framework and locked in this position by means of distance pieces. Accuracy of setting was checked by measuring the mutual inductance between *C* and *A*, *B* for a number of symmetrical positions of *C*, the coils *A*, *B* being sometimes in conjunction

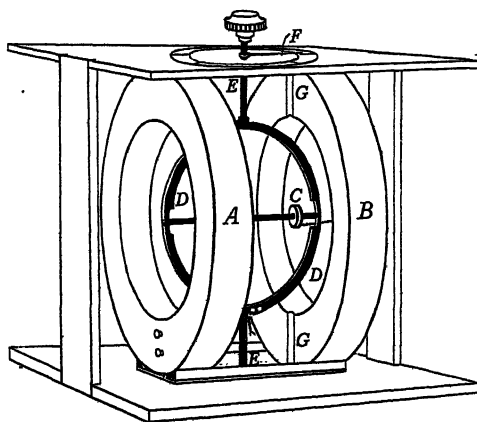


Figure 2.

and sometimes in opposition. The rod was then set at angles ranging from $\theta = 0^\circ$ to $\theta = 90^\circ$ inclusive, and a series of readings were taken of the mutual inductance M_j between *C* and *A*, *B* in conjunction for displacements varying from + 10 cm. to - 10 cm. They were measured on a Campbell mutual inductometer of range 0 to 11000 μH . either by Hartshorn's modification of Felici's a.-c. method* or by a d.-c. method with a ballistic galvanometer. A.-c. readings were standardized by comparison with occasional d.-c. readings. Figures 3 to 8 show M_j plotted against *l*, the displacement, for various angles θ and for separations of *A* and *B* ranging between 7.5 cm. and 20 cm. approximately.

The straightness of the lines obtained in figures 5 and 7 shows the constancy of M_j when θ and x/a are correctly chosen. This constancy is shown in a different way in figures 9 and 10, in which M_j is plotted against the angle θ for various displacements of *C*. The position of constancy for a value 0.089 of x^2/a^2 and the two positions of constancy for which $x^2/a^2 = 0.25$ are clearly shown. This method probably gives the more accurate way of judging the exact angle for which constancy of inductance is achieved. The actual figures taken show that for $x^2/a^2 = 0.25$ and

* *J. Sci. Inst.* 2, 145 (1925).

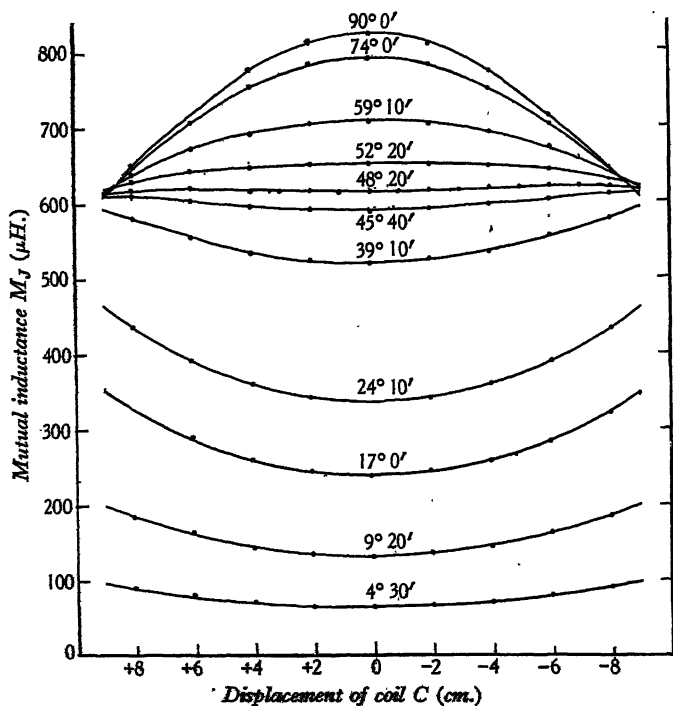


Figure 3. Coils *A* and *B* 7.40 cm. apart, in conjunction. $x^2/a^2=0.051$. *C* small.

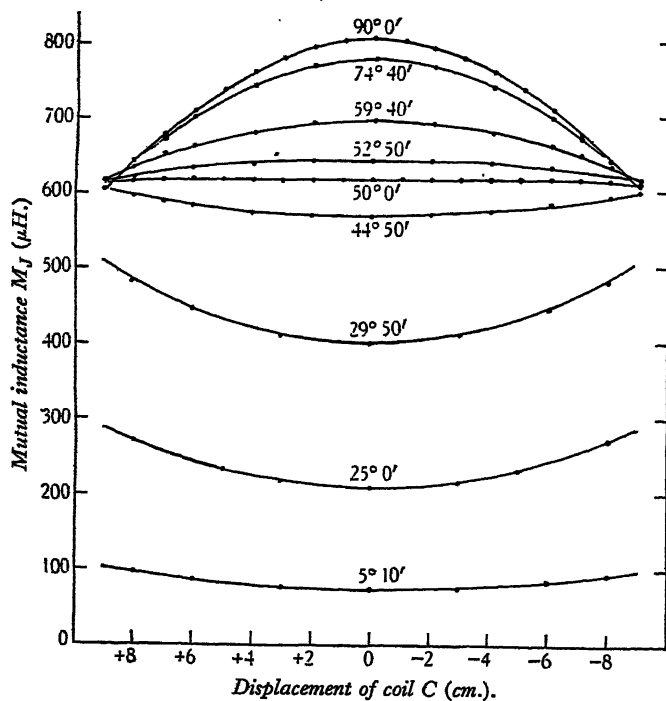


Figure 4. Coils *A* and *B* 8.48 cm. apart, in conjunction. $x^2/a^2=0.067$. *C* small.

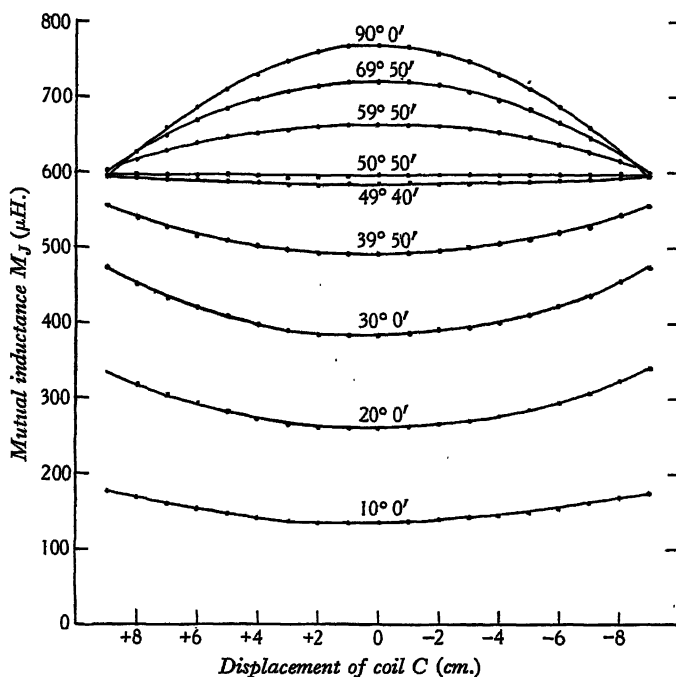


Figure 5. Coils *A* and *B* 9.81 cm. apart, in conjunction. $\kappa^2/a^2=0.089$. *C* small.

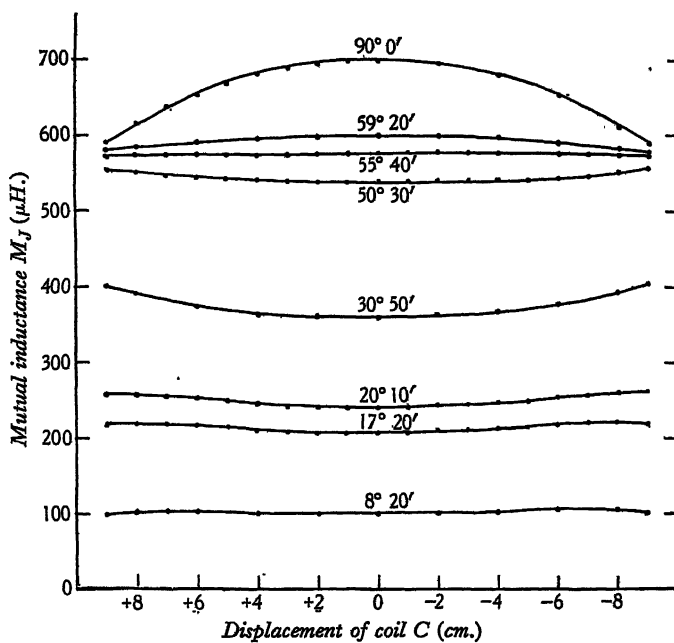


Figure 6. Coils *A* and *B* 13.1 cm. apart, in conjunction. $\kappa^2/a^2=0.159$. *C* small.

$\theta = 65^\circ$ or 33° the differences between the highest and the lowest readings were 0.65 and 1.6 per cent respectively over a range of ± 8 cm. Over the same range at $x^2/a^2 = 0.089$, $\theta = 51^\circ$, the difference was only 0.43 per cent. If in each case, to

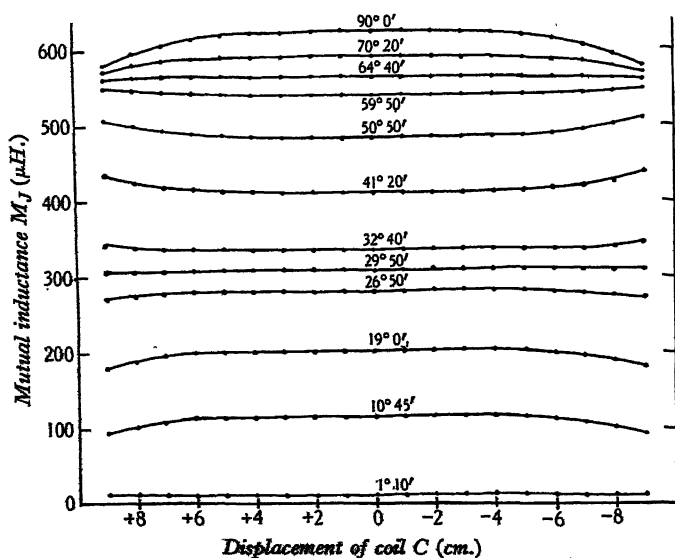


Figure 7. Coils *A* and *B* 16.4 cm. apart, in conjunction. $x^2/a^2 = 0.25$. *C* small.

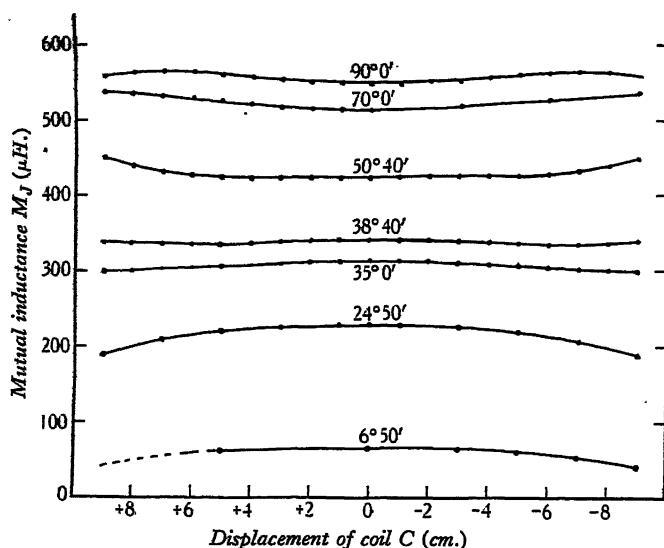


Figure 8. Coils *A* and *B* 19.8 cm. apart, in conjunction. $x^2/a^2 = 0.364$. *C* small.

obviate errors due to any lack of symmetry of setting, the average of the corresponding values on either side of zero is taken, the differences are only 0.45, 1.1 and 0.23 per cent respectively for the three values. The curves show that very approximate constancy of inductance over a more limited range of displacement is

achieved in other positions as a result of a rough balancing out of terms of opposite sign in equation (2) and that the angle for this position gets larger as the separation increases, while a second position of linearity appears after $x^2/a^2 = 0.16$ approxi-

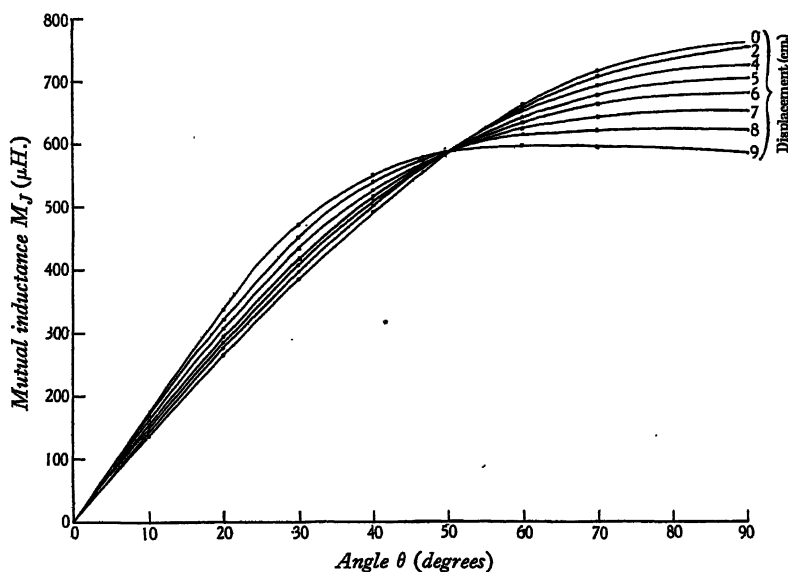


Figure 9. Coils *A* and *B* 9.81 cm. apart, in conjunction. $x^2/a^2 = 0.089$. *C* small.

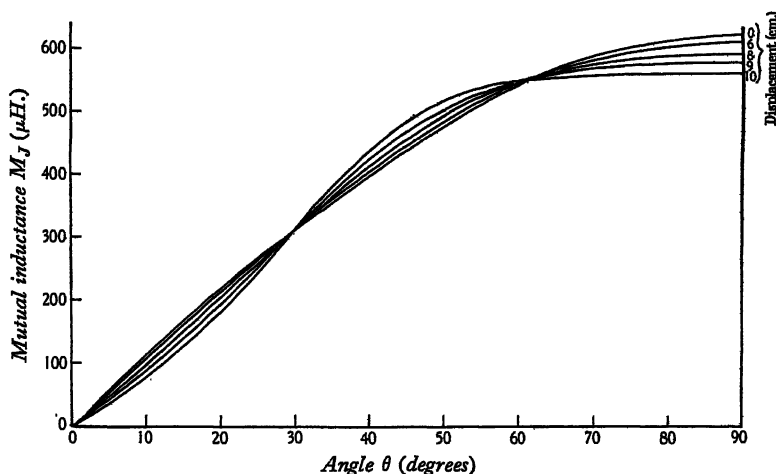


Figure 10. Coils *A* and *B* 16.4 cm. apart, in conjunction. $x^2/a^2 = 0.25$. *C* small.

mately. Theoretical considerations show that θ has risen to $50^\circ 46'$ when $x^2/a^2 = 1.41$, where a high order of constancy is again achieved. To complete the series, the apparatus was modified so that the rod *MN* passed through the centre of symmetry of the coil *A* alone. This corresponds to $x^2/a^2 = 0$, and figure 11 shows, as would be expected, that at this setting linearity is achieved over only a small range.

A further series of observations was taken in which the radius of C was not small compared with that of A or B . A coil of 200 turns of average diameter of 7.65 cm. and breadth 1 cm. was used. The separation chosen was that for

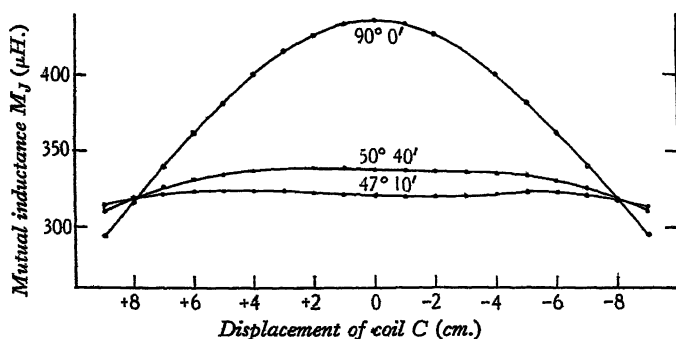


Figure 11. Coil A alone. $x^2/a^2=0$. C small.

$x^2/a^2 = 0.089$. Figure 12 shows that at about 50° , M_J is constant over a range of ± 7 cm. (A wider range could not be used owing to the presence of the circular framework.) The actual figures show a variation from highest to lowest of 0.44 per

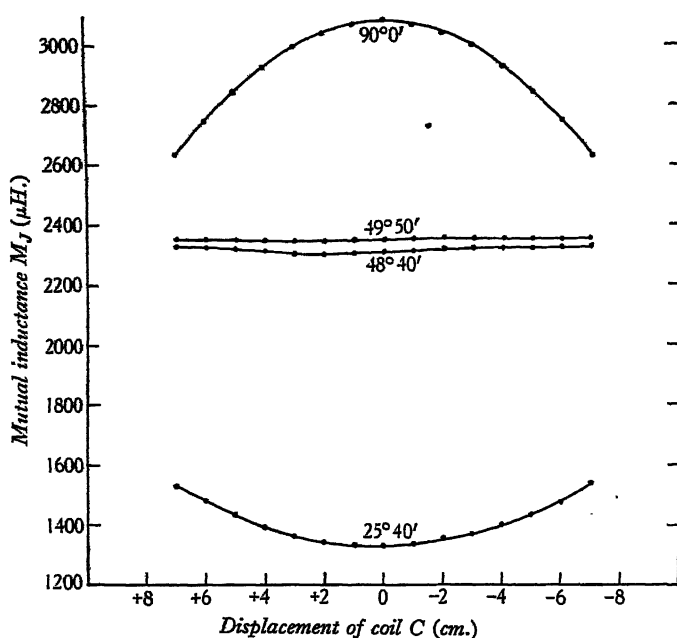


Figure 12. Coils A and B 9.81 cm. apart, in conjunction. $x^2/a^2=0.089$. C large.

cent. This experiment was not done under conditions of perfect symmetry for if the average of readings equidistant from zero be taken the variation is less than 0.1 per cent. It is shown in practice therefore that $M_\theta = GQ \sin \theta$ in such circumstances, even in the case of a large coil. Since, as was indicated in § 1, if a

magnet replaces the coil a similar expression is obtained for the flux threading A and B , the breadth and depth of such a magnet will not affect the accuracy of the expression for F in equation (10) so long as the magnet is lying along a line of isomutual inductance.

Measurement of the absolute moment of a magnet. An angle solenoid of length 3.9 cm. and consisting of 467 turns of double-silk-covered copper wire (s.w.g. 24) was inserted in a standard solenoid of known constant G_s , and the mutual inductance M_s between them was found. The solenoid was then mounted as shown in figure 13 on the circular framework previously used, and was so arranged that the centre of symmetry was at O for any angle θ made by its axis with the planes of A and B . This axis was then set to be perpendicular to A and B , the mutual inductance being zero as measured with a.-c. or d.-c., and a magnet was arranged by eye as symmetrically as possible within the solenoid so that its magnetic axis

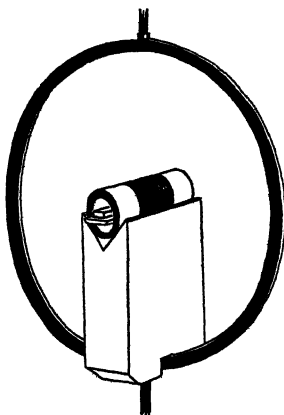


Figure 13.

coincided with the axis of the solenoid. The mutual inductance between solenoid and A , B in opposition was then not necessarily zero, owing to the disturbing influence of the magnet, but could be made zero by a slight shift of the magnet. A.-c. was used for the reading since direct currents might shift the magnet and would tend to demagnetize it. If the balance was not sharp in the position of zero inductance, a shift of the magnet along its axis combined with a slight rotation of it was made till the balance was sharp at zero. This indicated that the magnet was coaxial with the solenoid and symmetrically placed with respect to it. The leads to A and B in conjunction were then switched over to a Grassot fluxmeter and the closed circuit containing the angle solenoid was opened. The framework bearing the angle solenoid was swung round through the appropriate angle, according to the separation of A and B , so that the axes of solenoid and magnet lay along a line of isomutual inductance, and the resulting fluxmeter reading F was taken. The magnet was then withdrawn along its axial line till well out of the field of A and B and the fluxmeter reading was taken again. The coils were switched back to the inductometer and M_θ was measured. The average value of F/M_θ for the four sets

of readings corresponding to the four possible positions of the magnet was found and when substituted in equation (12) of § 1 gave the absolute moment of the magnet. The values obtained agreed within 1 per cent with values obtained by ordinary laboratory methods, but there was a marked gain in simplicity and the need for corrections for the length, breadth and depth of the magnet was avoided.

§ 3. EXPERIMENTS ON THE MUTUAL INDUCTANCE BETWEEN TWIN COILS IN OPPOSITION AND A SMALLER COIL

The apparatus. This was the apparatus described in the last section but the fields of *A* and *B* were in opposition. Figures 14 to 17 for the small coil and figure 18 for the coil of larger diameter show M_P plotted against l for various angles θ . For convenience the distances between *A* and *B* were the same as in § 2. For one of these $x^2/a^2 = 0.25$, figure 16. Now it is shown in § 1 that if $x^2/a^2 = 0.28$ then

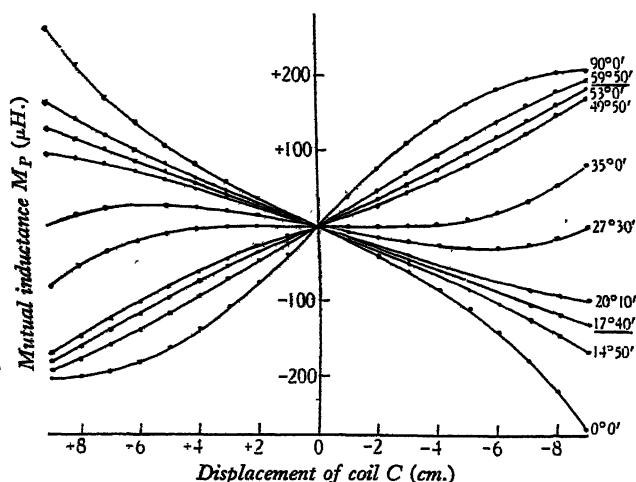


Figure 14. Coils *A* and *B* 9.81 cm. apart, in opposition. $x^2/a^2 = 0.089$. *C* small.

M_P/Gq is proportional to l for the angles $\theta = 19^\circ 53'$ and $\theta = 59^\circ 27'$. Although *A* and *B* were not at the ideal distance apart, the figure shows that straight lines were obtained. Moreover, equation (3) shows that if the second and third terms vanish by choice of θ and x/a respectively, then for the two suitable angles the ratio of the corresponding slopes dM/dl will be equal to $P_2(\sin 19^\circ 53')/P_2(\sin 59^\circ 27')$. This works out to be -0.53 . The ratio of the two slopes in figure 16 is -0.55 for a value of x/a smaller than it should be.

§ 4. EXPERIMENTS ON THE MUTUAL INDUCTANCE BETWEEN TWIN COILS IN CONJUNCTION AND A LARGE COIL ROTATING BETWEEN THEM

It has been shown* that for the case of two circles *A* and *B* arranged as in figure 1, and a coil *C* rotating about a diameter with its centre at *O*, where $l = 0$, the

* *Proc. Phys. Soc.* **44**, 200 (1932).

mutual inductance M between them can be made proportional to θ to a high order of accuracy. This theory, however, deals with circles, not multi-layered coils and the practical work set out in this paragraph was done with the object of showing

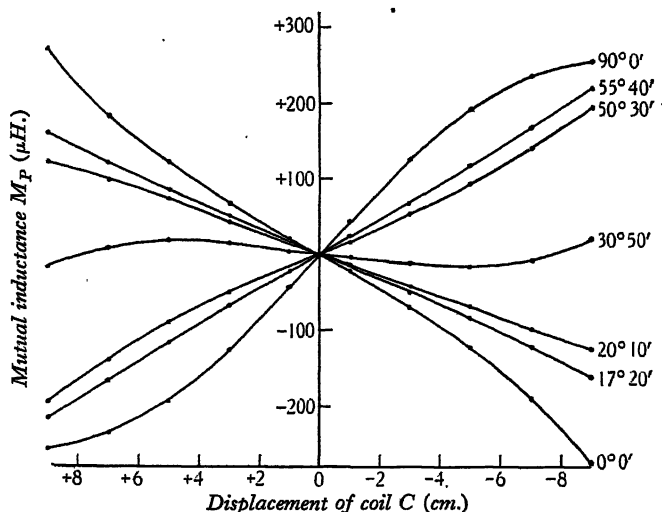


Figure 15. Coils A and B 13.1 cm. apart, in opposition. $x^2/a^2 = 0.159$. C small.

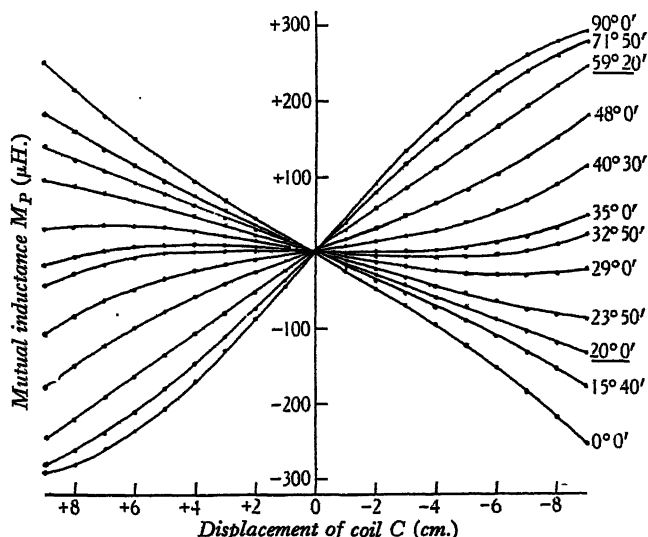


Figure 16. Coils A and B 16.4 cm. apart, in opposition. $x^2/a^2 = 0.25$. C small.

that the theoretical constancy of M/θ can be attained with multi-layered coils by arranging a suitable separation of A and B or by varying the radius of C .

The apparatus. The same twin coils A and B were used and were connected in conjunction. A large coil C was wound on a circular wooden former of diameter 18.55 cm. fitting inside an ebonite ring which pivoted on ebonite spindles about a vertical diameter passing through O . The centre of the wooden former was bored

so that an angle solenoid S consisting of 1360 turns of mean diameter 4.36 cm. could be inserted with its centre of symmetry at O , its windings being parallel to those of C . The number of turns of C was arranged so that the mutual inductances

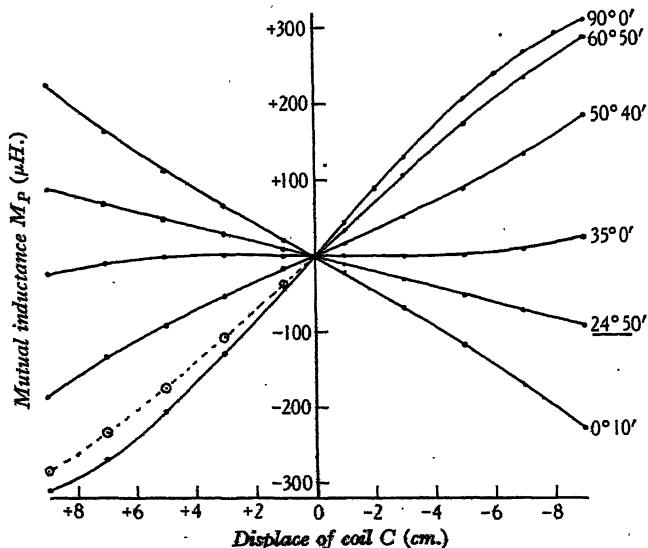


Figure 17. Coils A and B 19.8 cm. apart, in opposition. $x^2/a^2 = 0.364$. C small.

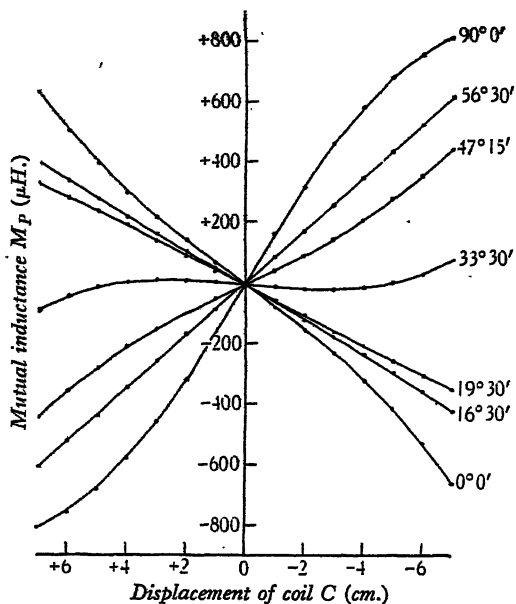


Figure 18. Coils A and B 9.81 cm. apart, in opposition. $x^2/a^2 = 0.089$. C large.

between A , B in conjunction and first C , then S , always involved the same thousands and the same hundreds studs of the mutual inductometer. In this way errors in the calibration of the inductometer were reduced to negligible proportions.

Method. In the first place, A and B were put as close together as possible and the mutual inductance M between these coils in conjunction and C , on the one hand, and the mutual inductance M_θ between A , B in conjunction and the angle solenoid on the other, were read for the same angle θ , for values between $+20^\circ$ and -20° . From M_θ , θ could be calculated and the variation of M with θ determined. It will be seen from column 1 in table 1 that as θ increased M/θ increased. A and B were then separated by about 3.5 cm. more and another set of readings was taken over the same range. Column 2 of table 1 shows that M/θ then decreased as θ increased. The coils were next put in an intermediate position, and column 3 of table 1 shows that in this case M/θ was practically constant. In order to show that proportionality between M and θ could be obtained by altering the radius of C instead of changing the separation of the coils in the first instance, another set of readings was taken for a smaller mean diameter of C . The coils A and B were practically in contact. It will be seen from column 4 of table 1 that M/θ showed a very small but definite decrease when θ increased. It is evident, therefore, that while in this last series the separation of A and B was slightly too large, or the mean radius of C slightly too small, these defects can be adjusted and constancy of the ratio M/θ is attainable in practice to a high degree of accuracy with multi-layered coils over a range of 20° on either side of zero.

Table 1

Approximate range of θ	Value of M/θ when			
	$x^2/a^2 = 0.0367$ $a^2/a^2 = 0.332$	$x^2/a^2 = 0.0893$ $a^2/a^2 = 0.332$	$x^2/a^2 = 0.0613$ $a^2/a^2 = 0.332$	$x^2/a^2 = 0.038$ $a^2/a^2 = 0.31$
$0^\circ 30' - 6^\circ 30'$	0.03487(5)	0.03348	0.03422	0.03445
$1^\circ 50' - 8^\circ 0'$	0.03488	0.03348	0.03422	0.03444
$3^\circ 20' - 9^\circ 40'$	0.03490	0.03347	0.03422	0.03444
$4^\circ 50' - 11^\circ 10'$	0.03491	0.03346	0.03422	0.03444
$6^\circ 30' - 12^\circ 50'$	0.03492	0.03344	0.03421(5)	0.03444
$8^\circ 0' - 14^\circ 20'$	0.03493	0.03342	0.03423	0.03443
$9^\circ 40' - 16^\circ 10'$	0.03494	0.03339	0.03422	0.03442(5)
$11^\circ 10' - 17^\circ 40'$	0.03495	0.03337	0.03422	0.03442
$12^\circ 50' - 19^\circ 20'$	0.03498	0.03335	0.03423	0.03442

§ 5. EXPERIMENTS ON THE USE OF AN ANGLE SOLENOID FOR THE MEASUREMENT OF AN ANGLE

The apparatus. That of the last section was used. Though the coil C was not needed, a slot was cut in its wooden former so that a plane mirror could be fixed with its reflecting surface on the axis of rotation. By means of a telescope and circular scale the angle through which the framework, and hence the angle solenoid, turned could be measured. It was sufficient to show that θ as calculated from $M_\theta/M_{90} = \sin \theta$ was proportional to the scale deflection since this, in its turn, was proportional to the angle in radians. Corresponding readings on either side of zero were (numerically) added to counteract any lack of symmetry of the scale and any uncertainty as to the true zero position due to irreversible inductance. The difference between each reading and the fourth reading below it in order was taken, giving a range of

approximately 20 cm. of scale. The maximum error in reading the scale may be taken as between 1 in 1000 and 1 in 2000. Within this degree of accuracy, the angle calculated from M_θ per cm. of the scale is constant, as is shown in table 2.

Table 2

$$x^2/a^2 = 0.0369.$$

Range of readings on scale (cm.)	44-30	40-26	37-23	34-15	30-8	26-3	23-0
Angle (sec.) per cm. of scale	521.3	521.3	521.3	521.4	521.7	522.0	521.0

The radius of curvature of the scale was just under 2 metres. As the range of angle tested in this series was only $5\frac{1}{2}^\circ$ on either side of zero, the calibration was tested over the wider range of $\pm 24^\circ$ of arc. For this, the angle solenoid S was set to give a small mutual inductance with A and B in conjunction and the mirror was arranged to give a scale reading of approximately -25 cm. S was then swung through a deflection corresponding to about 50 cm. of scale and the new inductance was noted. The deflection was such that this was just below $1000\mu\text{H}$. S was then arranged to give just over $1000\mu\text{H}$. and the mirror was arranged to give a reading at approximately -25 cm. again. When the solenoid was swung through an angle corresponding to 50 cm. of scale the inductance was then just under $2000\mu\text{H}$. Another set of readings was taken between $2000\mu\text{H}$. and $3000\mu\text{H}$. Corresponding readings were taken on the other side of zero mutual inductance by a similar method. This system of taking readings reduces errors in the calibration of the inductometer. The maximum error involved in scale estimation is about 1 part in 5000. Table 3 shows the maximum deviation from constant ratio is about the same.

Table 3

$$x^2/a^2 = 0.0380.$$

Angle covered (degrees)	$\frac{1}{2}-7\frac{1}{2}$	$8\frac{1}{2}-15\frac{1}{2}$	16-24
Angle (sec.) per cm. of scale	523.2	523.2	523.3

These figures show that it is sound in practice to use an angle solenoid to measure angles under 24° on either side of zero. Substitution of the actual values of the dimensions concerned shows that, either with the coils touching ($\psi = 79^\circ$) or in the Helmholtz position, $M_\theta/M_{90} = \sin \theta$ with an error not exceeding 1. part in over 10,000.

Throughout the whole of the practical work described in this paper, therefore, the theoretical expressions established for circles have been shown to apply in practice to multi-layered coils.

§ 6. ACKNOWLEDGMENT

The author wishes to express his gratitude to Dr H. R. Nettleton of Birkbeck College for making the suggestions which led to the work described here, and for the help that he has subsequently given.

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A TECHNIQUE FOR THE PHOTOGRAPHIC DETERMINATION OF THE INTENSITIES OF X-RAY REFLECTIONS FROM POWDERS

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ABSTRACT. A simple and accurate method of measuring the intensities of X-ray reflections from powders is described. The method consists in reflecting X rays from a plane, stationary layer of powder. Its special advantages are that the absorption factor can be very accurately obtained, and the variation of focusing across the film can be utilized to give lines of approximately the same blackness for reflections of widely different intensities. Three examples are given illustrating the use of the method for comparing reflections from mixed powders, for comparing widely different intensities, and for measuring intensities at large angles of reflection.

§ 1. INTRODUCTION

ALTHOUGH many methods have been used for the photographic recording of X-ray reflections from powders, the majority are more suitable for the measurement of the positions of the reflections than their intensities. For the determination of atomic scattering factors and for related investigations, intensity-measurements are essential and in connexion with such work we have been led to develop a technique which is both simple and accurate. The method is an adaptation of previous methods and utilizes certain features which have usually been regarded more as disadvantages than as advantages.

§ 2. SURVEY OF PREVIOUS WORK

The method most generally adopted is to have the powder in the form of a thin cylinder mounted at the centre of a cylindrical camera. This arrangement is well suited to the determination of the positions of lines, for they are all fairly sharply defined and, within limits, are equally sharp for all angles of reflection. The chief difficulty encountered in measuring intensities by this method is the accurate determination of the absorption factor for a cylindrical specimen. This has been considered by Claassen* and subsequently by Rusterholz†. The absorption factor involves the linear absorption coefficient of the powder in the cylinder

* A. Claassen, *Phil. Mag.* 9, 57 (1930). See also P. Debye and P. Scherrer, *Phys. Z.* 19, 474 (1918); G. Greenwood, *Phil. Mag.* 3, 963 (1927).

† A. A. Rusterholz, *Z. f. Phys.* 63, 1 (1930).

and this is difficult to obtain accurately. Furthermore, the comparison of reflections of widely different intensities by this method is not easy, for since all the lines are more or less equally well focused, it is necessary to make the strong lines very black in order to bring out the weak ones; errors are then likely to arise when the blackness of the film measured with a photometer is converted to X-ray intensities by means of a calibration curve.

Several methods have been based on the use of a flat layer of powder. If the incident and reflected X-ray beams are equally inclined to the surface of the powder, the expression for the absorption coefficient* is simple and it can be accurately determined. Moreover, the reflected beam is sharply focused, provided the distances from the powder to the film and to the point of divergence of the incident X rays are equal. This method is frequently used in conjunction with the ionization spectrometer because the plate of powder can always be set at the correct angle for each reflected beam, but it is not generally used with photographic recording because many reflections are recorded simultaneously and it is only over a narrow range of angles that there is sharp focusing. This aspect of the matter has been discussed in detail by Brentano† who has designed an X-ray camera which overcomes this drawback by means of a slit moving across the photographic film; the motion of the slit is coupled with that of the powder in such a way that as the powder rotates the lines which are recorded on the film are always sharply focused. In designing this camera, Brentano has been concerned primarily with the measurement of the positions of X-ray reflections and his arrangement is almost equivalent to an ionization spectrometer as regards its focusing properties. In later papers, Brentano‡ shows that this form of camera can also be used for measuring the intensities of reflections and he gives an expression for the absorption factor for X rays reflected from a flat plate.

In our own experiments, a stationary plate method has been finally adopted without the refinements of the Brentano camera. The geometrical simplicity of the method allows the absorption factor to be calculated easily and accurately while the lack of sharp focusing at all points of the film is no disadvantage when intensities alone are required and has actually proved to be a most useful feature of the method.

§ 3. DETAILS OF THE PRESENT METHOD

The camera. A diagram of the camera is given in figure 1. It consists of a stout-walled brass cylinder, 6 cm. in diameter, lined internally with lead. The powder is mounted in a holder attached to a central rod and its position can be read off on a circular scale on the top of the camera. The X-ray beam is collimated by a cylindrical tube, 2 cm. long and 0.7 mm. in diameter, pointing directly at the axis of the camera. The powder is contained in a cavity in a block of mild steel, machined so that its face is accurately plane and lies exactly on the axis of the camera when mounted in position. The cavity is approximately 2.5 cm. long, 1 cm.

* See A. H. Compton, *X-Rays and Electrons*, chap. v (Macmillan and Co. Ltd., London, 1927).

† J. Brentano, *Proc. Phys. Soc.* 37, 184 (1924).

‡ J. Brentano, *Phil. Mag.* 4, 620 (1927); 6, 178 (1928).

wide and 1.5 mm. deep; these dimensions ensure that the whole of the incident beam falls on the face of the powder, that the reflected beams emerge from this face and that for most substances the thickness is effectively infinite. The area of powder irradiated is of the order of 1 to 3 mm.² depending on the setting of the plate with respect to the incident beam. The reflections pass through a horizontal slit in the wall of the camera and fall on a photographic film wrapped round the outside.

Determination of the setting of the powder-holder. The determination of the angle α , figure 1, is important in the calculation of the absorption factor, and an accuracy of 0.2° is necessary for this purpose. A direct X-ray method was found

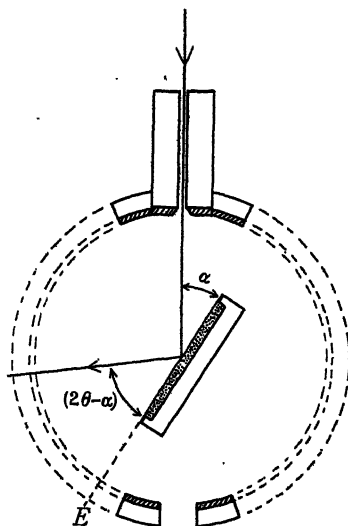


Figure 1. Diagram of the camera.

to be sufficiently accurate. By considerably over-exposing the photograph, a sharp edge in the general background is cast by the powder-holder at the point *E* on the film. Measuring the position of *E* with respect to the lines on the photograph leads to a direct determination of the angle α . This method is preferable to geometrical or optical methods because it gives the position of the powder-holder with respect to the actual path of the incident X-ray beam.

§ 4. THE INTENSITY OF REFLECTION OF X RAYS FROM POWDERS AND FROM MIXTURES OF POWDERS

The theory of reflection of X rays from crystalline powders has been fully dealt with elsewhere* and it will only be necessary here to adapt the results to the present experimental arrangement. The usual way of obtaining *absolute* values for reflections from powders is to compare the intensities reflected from the substance under investigation with the intensities from a standard substance, usually NaCl,

* See A. H. Compton, *loc. cit.*

KCl or aluminium, which have already been measured absolutely by other methods*. The two substances are finely powdered and intimately mixed to form a composite plate of powder having an average linear absorption which can be taken to be the same for reflections from the two powders†. A formula will now be developed comparing the intensities I_1 and I_2 of two reflections from powders 1 and 2 respectively.

The integrated reflection dI from a small volume dV containing randomly orientated crystals of one kind is given by Compton in the following form:

$$\frac{dI}{I} = \frac{N^2 \lambda^3}{2} \cdot \frac{e^4}{m^2 c^4} \cdot F^2 \cdot \left(\frac{1 + \cos^2 2\theta}{\sin 2\theta} \right) \cdot \frac{pl}{8\pi Sr \cdot \sin \theta} \cdot dV \quad \dots\dots(1),$$

where

I is the intensity of the incident beam;

S the area of the incident beam;

r the distance of the film from the crystal holder;

l the length of the line recorded on the film;

p the multiplicity factor for the reflection;

N the number of unit cells per unit volume of the crystal‡;

F the amplitude scattered per unit cell in terms of the amplitude scattered by a single electron;

and λ , e , c , m , θ have their usual significations.

When reflection takes place from a plate of powder, the effective volume element becomes $dV (\rho'/\rho)$, where ρ' is the effective density of the substance in the plate and ρ is the true density of the substance itself. With the present experimental arrangement it is convenient to take for the volume element, the powder irradiated lying between depths x and $(x + dx)$. It may then easily be shown that

$$dV = \frac{S \cdot dx}{\sin \alpha} \cdot \frac{\rho'}{\rho} \quad \dots\dots(2),$$

where α is the angle between the incident beam and the surface of the powder, figure 1. Combining equations (1) and (2) and grouping all the constant terms together, we have

$$dI = (\text{constant}) \cdot p \cdot N^2 \cdot F^2 \left(\frac{1 + \cos^2 2\theta}{\sin \theta \cdot \sin 2\theta} \right) \frac{\rho'}{\rho} \cdot \frac{dx}{\sin \alpha}.$$

The total reflected intensity, I_r , is obtained by integrating this equation from $x = 0$ to $x = \infty$, and taking into account the absorption of the incident and reflected X rays for each layer dx . A little consideration shows that for a layer of powder at a depth x the incident rays traverse a distance, $x/\sin \alpha$ and the reflected

* R. W. James and E. M. Firth, *Proc. R.S. A* 117, 62 (1927); R. W. James and G. W. Brindley, *Proc. R.S. A* 121, 155 (1928); R. W. James, G. W. Brindley and R. G. Wood, *Proc. R.S. A* 125, 401 (1929).

† The conditions under which this holds are discussed in § 5.

‡ Compton obtained equation (1) by considering a simple cubic lattice containing atoms of only one kind. In extending this result to crystals of other kinds, N and F apply to the unit cell of the structure and have the definitions given above. This point has often been overlooked in carrying over Compton's notation to the general case.

rays a distance $x/\sin(2\theta - \alpha)$ in the powder, so that the total distance in the powder is

$$\{x/\sin \alpha + x/\sin(2\theta - \alpha)\}.$$

The total intensity reflected from the block of powder is therefore given by

$$I_r = (\text{constant}) \times \frac{pN^2F^2}{\sin \alpha} \left(\frac{1 + \cos^2 2\theta}{\sin \theta \sin 2\theta} \right) \frac{\rho'}{\rho} \int_{x=0}^{x=\infty} e^{-\mu' \{x/\sin \alpha + x/\sin(2\theta - \alpha)\}} dx,$$

where μ' is the coefficient of linear absorption for the powder. Evaluating the integral, we have finally

$$I_r = (\text{constant}) pN^2F^2 \left(\frac{1 + \cos^2 2\theta}{\sin \theta \sin 2\theta} \right) \frac{\rho'}{\mu' \rho} \left[\frac{\sin(2\theta - \alpha)}{\sin(2\theta - \alpha) + \sin \alpha} \right].$$

The expression in the square brackets is the absorption factor for a plate which is effectively of infinite thickness, and its value is independent of the actual value of μ' . This is an important advantage of the plate method as compared with the cylindrical-rod method, because in comparing the intensities of two reflections from a plate it is not necessary to know the linear absorption of the powder. The last equation may be written more conveniently as follows:

$$I_r = (\text{constant}) \cdot p \cdot N^2 \cdot F^2 \cdot \phi(\theta) \cdot A \cdot \rho' / \rho \quad \dots\dots(3),$$

where $\phi(\theta)$ includes all the trigonometrical functions and A is the absorption factor. This expression for A is essentially the same as that given by Brentano*.

When relative values of F for a single substance are required, equation (3) reduces to the following simple form:

$$I_r = (\text{constant}) \cdot p \cdot F^2 \cdot \phi(\theta) \cdot A \quad \dots\dots(4).$$

When a mixture of two powders is considered†, the form of equation (3) may be modified in the following way. The effective density ρ' is proportional to G , the weight of the reflecting substance present in the mixture. The true density ρ can be written as $M \cdot m_H / a^3$, where M is the total molecular weight of the unit cell, m_H is the mass of the hydrogen atom, and a^3 is the volume of the unit cell if the latter is assumed to be cubic; otherwise, the correct expression for the volume of the cell must be used in place of a^3 . Also, $N = 1/a^3$. Substituting these results with the appropriate suffixes in equation (3), we obtain finally

$$\frac{I_1}{I_2} = \frac{p_1 \cdot F_1^2 \cdot \phi_1(\theta) \cdot A_1 \cdot G_1 \left(\frac{a_2}{a_1} \right)^3 \frac{M_2}{M_1}}{p_2 \cdot F_2^2 \cdot \phi_2(\theta) \cdot A_2 \cdot G_2 \left(\frac{a_2}{a_1} \right)^3 \frac{M_2}{M_1}} \quad \dots\dots(5).$$

In this equation (I_1/I_2) is the ratio of the intensities of two reflections as measured by the method described above. If F_1 is the amplitude reflected by a unit cell of the standard substance, NaCl, KCl, or Al, then the equation can be used to measure F_2 , the amplitude reflected by a unit cell of the substance being investigated.

* *Loc. cit.*

† For an intimate mixture of two powders, a common value of μ' may be assumed.

§ 5. THE PREPARATION OF SATISFACTORY BLOCKS OF POWDER

In our experiments we have sometimes found it surprisingly difficult to obtain really satisfactory blocks of powder. Before equations (4) and (5) can be applied it is essential to ascertain whether the conditions postulated in deriving equation (1) are satisfied, viz., that the powder consists of a random arrangement of very fine particles.

Difficulties may arise in several ways in obtaining a random distribution of the particles. If the particles are flat or elongated or of a flaky nature they are almost certain to have a preferential orientation in the powder; we have found that this happens with commercial aluminium powder and the intensities obtained from such a powder are not in the same ratio as if the particles were randomly distributed. If the lines of the X-ray photographs show any trace of individual spots and are not continuously black, then the particles are evidently so large that reflection occurs only along certain directions depending on the way in which the individual particles are arranged. Photographic methods have an important advantage here over ionization methods, because spottiness of the lines might very easily be overlooked in the latter method.

The maximum particle-size which can be tolerated in a powder depends on the substance and on the radiation. Quite roughly one may say that at least half the radiation falling on a particle must pass through it in order that a sufficient number of particles may be irradiated. Assuming the usual equation for X-ray absorption, $I = I_0 e^{-\mu x}$, where I is the intensity transmitted through a thickness x , μ is the linear absorption coefficient and I_0 is the incident intensity, and taking I/I_0 to be not less than $\frac{1}{2}$, we have that x must be not greater than $(\log_e 2)/\mu$, i.e., x must be less than $0.7/\mu$ approximately. In the case of copper K_α radiation reflected from aluminium and from copper, the particle-sizes must be less than about 50×10^{-4} cm. and 15×10^{-4} cm. respectively. In this example the radiation will penetrate effectively four or five layers of particles and if 1 mm² of the powder surface is irradiated about 2000 aluminium particles or about 10,000 copper particles will contribute to the reflection. In this connexion it may be mentioned that the plate method is superior to the cylindrical-rod method in that it allows a much larger volume of powder to be irradiated; more particles take part in the reflection and it is therefore easier to satisfy the requirement that the particles shall be randomly distributed.

The preparation of sufficiently fine particles sometimes presents difficulty and no general rules can be given. But it may be well to point out that in the case of metals and alloys, where the usual practice is to obtain the powder by filing and sieving through a fine-meshed gauze, the process of filing may affect the intensities of reflection as a result of distortions produced in the metal; we shall discuss this in detail elsewhere. In the case of potassium chloride we have found that repeated grinding by hand in a mortar will not give sufficiently fine particles; in such a case chemical methods may be used.

In comparing reflections from mixed powders, even greater care must be taken

to obtain suitable particles. If the sizes and absorption coefficients of the two kinds of particles are approximately the same, then the equations in § 4 are applicable, but when these conditions are not satisfied the question of the absorption in a composite block of powder must be considered in more detail. In such a case, an average absorption coefficient for the whole powder cannot be assumed and allowance must be made for the distribution of the two kinds of particles. This has been carefully worked out by Schäfer* for the case of copper K_{α} radiation reflected from a mixture of aluminium and iron for which the linear absorption coefficients are respectively 130 and 2600. In this somewhat extreme case the equations in § 4 are only applicable if the particle-size is of the order of 10^{-5} cm.

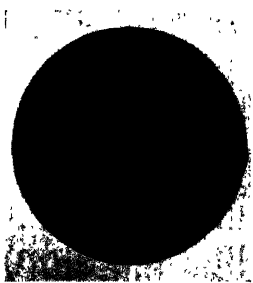


Figure 2. Microphotograph of Cu-KCl mixture. (Magnification 80 diameters.)

It is not always easy to prepare a satisfactory mixture of two constituents. Metals, such as aluminium and copper, mix readily but a metal and a powder such as potassium chloride are more difficult to mix. In the latter case the process is facilitated by adding a small quantity of alcohol and stirring continually while the alcohol evaporates; when the mixture becomes pasty it is transferred to the powder-holder and the surface is smoothed quite flat with a glass plate. When the mixture is dry, a perfectly smooth surface is obtained which does not crack. Figure 2 shows a microphotograph of a Cu-KCl mixture obtained in this way.

§ 6. THE ABSORPTION FACTOR AND THE QUESTION OF FOCUSING THE REFLECTED BEAMS

The absorption factor A has been shown to be given by the equation

$$A = \left[\frac{\sin (2\theta - \alpha)}{\sin (2\theta - \alpha) + \sin \alpha} \right] \quad \dots\dots(6).$$

If the plate is set so that the incident and reflected beams make equal angles with the surface of the powder, then $\theta = \alpha$ and the expression for A reduces to $\frac{1}{2}$; substituting this special value of A in equation (3) we have the usual expression for the intensity of reflection from a powder as it is generally measured with an ionization spectrometer. Furthermore, if the distances from the powder to the

* K. Schäfer, *Z. f. Phys.* 86, 738 (1933).

film and to the source of X rays are equal, then the condition $\theta = \alpha$ is also the condition for sharp focusing of the reflected beam.

It is most important in using the present method to have a clear picture of how the absorption factor and the focusing effect are related and of their bearing on the shape and intensity of the lines recorded on the photographic film. Suppose that, as often occurs in practice, we wish to compare two reflections, a strong reflection a at a small angle θ_a and a comparatively weak reflection b at a larger angle θ_b . If the powder plate is set so as to focus b sharply, then α must be made approximately equal to θ_b and A_b will be about 0.5. Under these conditions the strong reflection a will be much less sharply focused than b , and A_a will be less than A_b and may be about 0.2 or 0.3. Thus, by choosing the geometrical conditions rightly, the strong reflection can be reduced by absorption and can be broadened by the absence of sharp focusing, with the result that the lines a and b recorded on the photographic film may both be approximately of the same blackness. It is not at all essential when intensities are being measured that the lines should be sharply or equally focused; it is very much more important that they should be of about the same degree of blackness, so that the maximum accuracy can be obtained when the film is photometered. The variation of focusing produced by a stationary plate has hitherto been regarded as a disadvantage, and it is a disadvantage when the positions of lines are required accurately, but when intensities are required it is definitely an advantage.

In practice it is very useful to have a large-scale diagram of A plotted against θ for a series of values of α changing by 5° at a time; a graph of this kind is shown in figure 3. In using the diagram it should be remembered that the horizontal line through $A = 0.5$ corresponds to $\theta = \alpha$ which is the condition for sharp focusing.

When reflections from a mixture of two powders are to be compared, the method is particularly adaptable, for there are three factors by which the photographic densities of the lines can be controlled, viz., the composition of the mixture, the absorption factor, and the focusing-effect.

§ 7. PHOTOGRAPHY AND PHOTOMETRY

To secure uniform development, the films were mounted vertically in the developer and were kept in motion by a simple mechanical arrangement. They were calibrated directly in terms of X-ray intensities by means of a step wedge in the manner described by Bouwers*. It has previously been shown† that the density is directly proportional to the X-ray intensity up to a certain point depending on the nature of the film; this limit is at a density about 1.0 above the unexposed part of the film for the Agfa-Laue films used in our experiments. It is usually possible to keep the densities of the lines below this limit so that the calibration curve connecting intensity with photographic density need not be used in obtaining

* A. Bouwers, *Physica*, 3, 113 (1923).

† G. W. Brindley and F. W. Spiers, *Phil. Mag.* 16, 686 (1933). References to earlier work will be found in this paper.

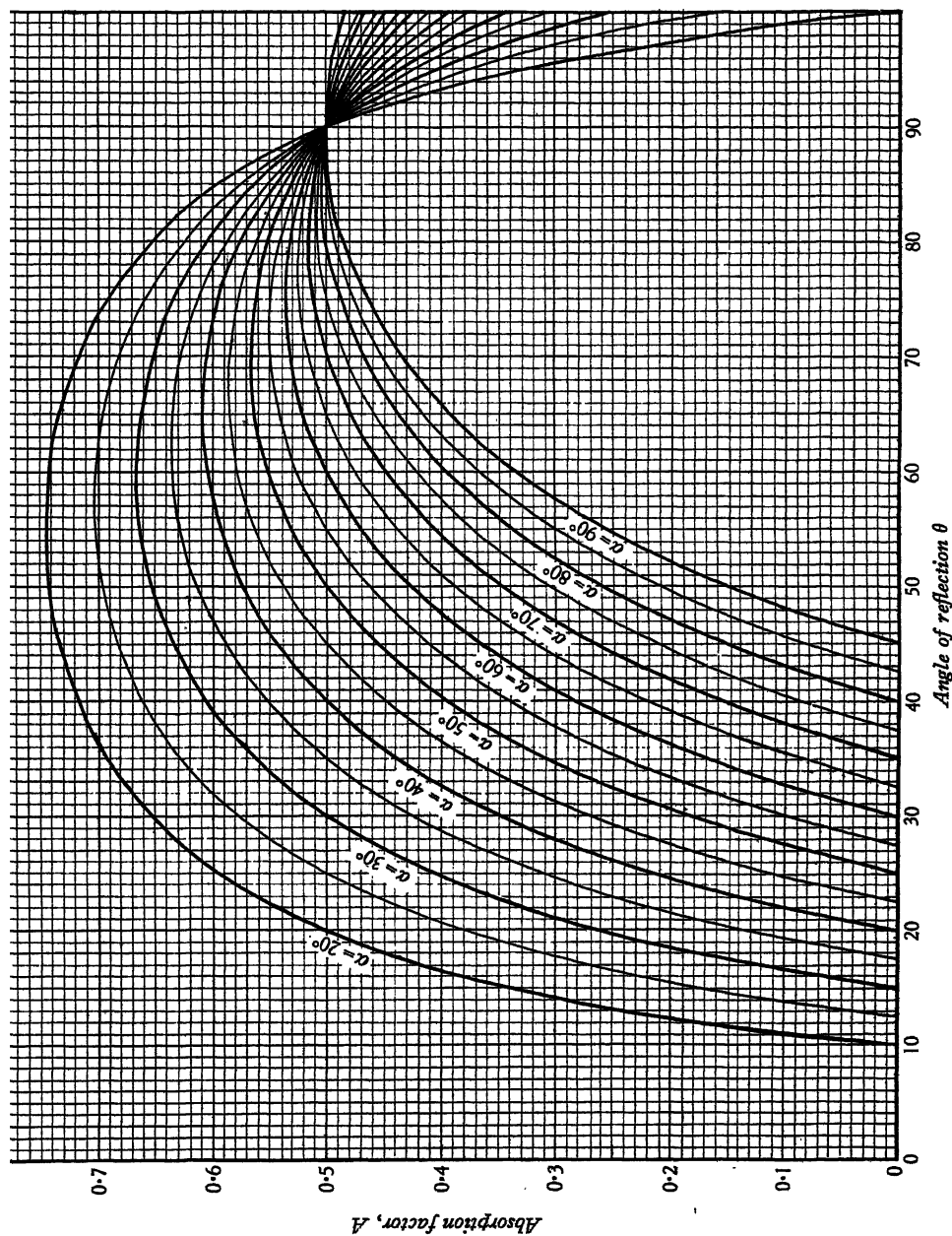


Figure 3. The absorption factor A plotted as a function of θ and α .

relative intensities; it is, however, a useful safeguard to have this calibration wedge on every film.

The films are most satisfactorily photometered by a null method which determines the densities directly in terms of a calibrated photographic wedge. The lines are then plotted out on squared paper and the areas above the general background taken as measures of the integrated reflections. Background variation due to the grain-size of the film is the chief source of error in determining these areas. For lines of medium intensity the error is quite small but becomes a serious matter for very weak reflections. Hence it is advantageous to have a method by which the energy of a weak reflection can be concentrated into a narrow line standing well above the background. Figure 4 shows two reflections from a mixture of

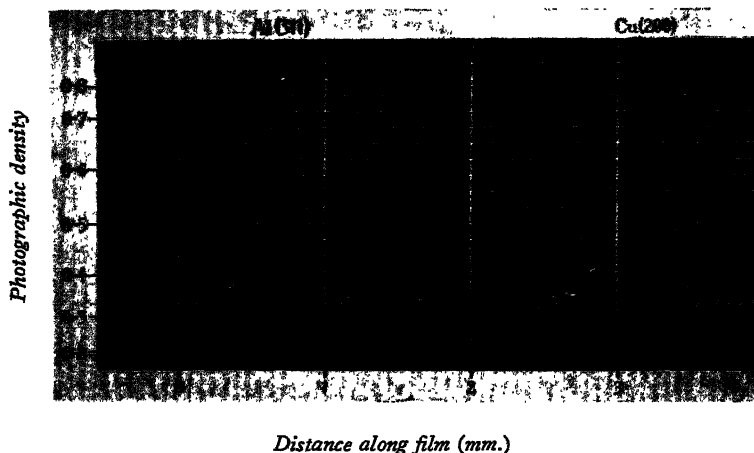


Figure 4. Microphotometer trace of Cu (220) and Al (311) reflections from mixed copper and aluminium powders.

copper and aluminium taken with a Cambridge recording micro-photometer*; the two reflections are Cu (220) and Al (311). The background variations shown in this figure are typical of a rather coarse-grained X-ray film; finer-grained films give slightly smaller variations, but the increase in accuracy is small and in general does not justify the much longer exposures which are necessary.

§ 8. TYPICAL RESULTS

Finally we shall give three examples to show how the method works in actual practice.

Example (1). Table 1 illustrates the use of the method in comparing reflections of widely different intensities from a single substance.

The figures in the last two columns of Table 1 show that although the values of $pF^2 \cdot \phi(\theta)$ for these three reflections are approximately in the ratio 5 : 2 : 1, the actual intensities which have to be measured are almost equal as a result of choosing

* This instrument was purchased out of a grant made to Prof. Whiddington by the Royal Society.

an appropriate value for α . Moreover, the very strong (111) reflection is not focused so well as the (220) reflection and, as a result of this, the photographic densities for these reflections are practically equal.

Table 1. Data for the intensity of reflection of copper $K\alpha$ radiation from copper powder

Reflection	2θ	α	$(2\theta - \alpha)$	A	Relative intensities from films $pF^2 \cdot \phi(\theta) \cdot A$	Relative values of $pF^2 \cdot \phi(\theta)$
(111)	$43^\circ 20'$	$37^\circ 18'$	$6^\circ 2'$	0.148	141 ₈	474
(200)	$50^\circ 28'$	„	$13^\circ 10'$	0.273	106 ₀	193
(220)	$74^\circ 8'$	„	$16^\circ 50'$	0.497	100	100

Example (2). Table 2 shows the accuracy with which reflections from mixed powders can be measured.

Table 2. Comparison of KCl (420) and KCl (422) + Cu (220) for copper $K\alpha$ radiation

Film ...	660a	660b	661a	661b	662a	662b	663a	663b	
KCl (420)	678	601	808	680	641	581	670	838	Areas
KCl (422) + Cu (220)	1220	1135	1475	1246	1231	1118	1282	1556	
KCl (420)	100	100	100	100	100	100	100	100	Relative intensities
KCl (422) + Cu (220)	180	189	183	183	192	192	191	186	

Average results: $\frac{\text{KCl (420)}}{\text{KCl (422) + Cu (220)}} = \frac{100}{187}$

These results show the order of accuracy which is obtainable in measuring relative intensities photographically. The variation of the individual values about the mean value is due partly to inhomogeneities in the films themselves and partly to small uncertainties arising from the grain-size of the films. Complete agreement between the results from a series of films cannot be expected, but when an average is taken of the results yielded by six or eight films the error is not likely to be large in the final result; the results given in the next example support this statement.

Example (3). Table 3 shows the accuracy which can be obtained at large angles of reflection, where the increase of general scattering makes the determinations much more difficult than at small angles of reflection.

In the first part of table 3 we give the necessary data for calculating the relative values of $pF^2 \cdot \phi(\theta) \cdot A$ for four reflections of copper $K\alpha$ radiation from aluminium powder. The F values used were interpolated from those obtained by James, Brindley and Wood* for a large single crystal of aluminium. The second part of the table gives the relative intensities measured from 14 films. The probable error

* Loc. cit.

in the last column was obtained as follows. If r is the difference between an actual value and the mean value, then the probable error is taken as $\sqrt{(\sum r^2)/n}$, where n is the number of observations*. The agreement between the observed and the calculated values is very satisfactory and shows that the present method of measuring intensities is reliable provided that the average of a sufficient number of films be taken.

Table 3. Data for the intensity of reflection of copper $K\alpha$ radiation from aluminium powder

(1) Calculated values of relative intensities from equation (4)

Reflection	2θ	α	$(2\theta - \alpha)$	A	p	F^2 (James and Brindley)	ϕ (θ)	$pF^2 \cdot \phi$ (θ) $\cdot A$ (relative values)
(311)	$78^\circ 22'$	$61^\circ 24'$	$16^\circ 58'$	0.249	24	33.5	1.683	118.1
(331)	$112^\circ 10'$	—	$50^\circ 46'$	0.468	24	17.1	1.486	100.0
(420)	$116^\circ 46'$	—	$55^\circ 22'$	0.484	24	16.0	1.582	102.8
(422)	$137^\circ 44'$	—	$76^\circ 20'$	0.525	24	11.5 ₈	2.467	125.8

(2) Observed values of relative intensities

Reflection	Observed relative intensities. Mean values for 14 films	R.m.s. error
(311)	118 ₅	$\pm 1_0$
(331)	100	± 0
(420)	104 ₀	$\pm 1_0$
(422)	126 ₀	$\pm 1_5$

This last example is a fairly stiff test of the method because it involves reflections over a wide range of angles, from 78° to 137° , a wide range of absorption factors, and a fairly large variation in the degree of focusing. The angle α was chosen to be about 60° so as to obtain good focusing for the (420) and (422) reflections; these are more difficult to measure owing to the partial resolution of the $K\alpha_1$ and $K\alpha_2$ lines. The (311) reflection is much stronger than the others because of the much larger value of F^2 , but it was cut down by the absorption factor and by broad focusing, so that it appeared on the films with about the same degree of blackness as the other lines.

§ 9. ACKNOWLEDGMENTS

Finally we wish to thank Professor Whiddington for his interest in these experiments and the Government Grant Committee of the Royal Society for a grant with which some of the necessary apparatus was bought.

* See A. S. Eddington, *Proc. Phys. Soc.* 45, 271 (1933).

A SELF-SYNCHRONIZED SYSTEM FOR IONOSPHERIC INVESTIGATION BY THE PULSE METHOD

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ABSTRACT. The paper describes an arrangement for the convenient study of the ionosphere by the pulse method when the sending and receiving stations are of necessity in different locations having no interconnection (e.g. no common mains supply) to provide a synchronizing-frequency.

Even under conditions of considerable electrical interference, the system provides (a) an extremely steady pattern of layer-height and echo-intensity on the cathode-ray oscillograph screen, suitable for visual observation or for photographic snapshot records; (b) immediate photographic delineation of a curve showing the variation of layer-height with frequency; and (c) continuous records of the variation of layer-height with time. It has the advantage that local disturbances connected with the mains supply do not produce a stationary pattern on the screen, as is the case when the pulse-recurrence frequency is the same as that of the mains supply at the receiver.

A very simple and positive method of modulating a pulse transmitter, which uses a thyratron alone without the usual amplifying or auxiliary control valves, is described.

A further innovation is that the calibration of the time base or scale of equivalent height is impressed permanently on the record, thus providing a continuous check of scale value, and facilitating the interpretation of the records.

§ 1. THE GENERAL PROBLEM

IN the usual application of the group-retardation method of Breit and Tuve⁽¹⁾ for the investigation of the ionosphere, successive pulses of radio-frequency energy are radiated at regular intervals and (after suitable treatment at the receiver) are exhibited, together with any echoes which may be reflected from the upper atmosphere, on a cathode-ray oscillograph or similar device. This delineation at the receiver is usually accomplished by using a time base whose recurrence frequency can be kept the same as that of the received pulses. The pulses cause deflections of the oscillograph spot at right angles to the sweep of the time base, and since the echo is delayed with respect to the ground pulse it is relatively displaced on the time base, giving the now familiar echo pattern. If any exhaustive study is to be made of the heights of return and the intensities of the echoes, this pattern should remain extremely steady over long periods and under varying conditions quite automatically, otherwise the labour of manipulation becomes excessive.

Consider the steadiness in position required for the different types of records taken in these investigations. For snapshot work, the time during which the pattern

should remain stationary need be no longer than $\frac{1}{2}$ sec., though, where the general noise is considerable, much better discrimination can be obtained by exposures of 1 sec. or more. Provided that the frequency and phase of occurrence of the pulse are reasonably steady this presents little difficulty, for the frequency of recurrence of the time base can be made equally steady. For P', f curves, showing the relation between the equivalent path P' and the frequency f , where the time spent on each frequency must be reduced to a minimum to obviate variations of height with time, the main requirements are that the pattern shall take up its position as soon as possible and that it shall remain stationary long enough to be photographed. Further, since one snapshot cannot be regarded as a fair sample of the conditions for that frequency, several such pictures, or their equivalent, are required. This entails constancy in position over a period of some 15 sec., and to attain this we must have considerable stability in both the pulse and time base recurrence-frequencies, together with rapidity of phase adjustment or, better still, automatic phase adjustment.

For P', t curves, i.e. curves showing the variation of the equivalent path with time, conditions are much more stringent. The pattern must remain in the field of the camera indefinitely, and any unavoidable variation in position must be small and gradual. The amount of variation which can be allowed depends mainly on one's personal idea of a good record, but it should at most be less than one-fifth of the distance between the ground pulse and the first echo. Thus there must be not only frequency stability in the two recurrence-frequencies but also accurate phase-control, for the relative phase must not vary by more than a degree or two.

Consider now the influence of local conditions at the transmitter and receiver. When a suitable common frequency is already available at both, the problem almost resolves itself. The simplest arrangement is that in which the same a.-c. mains supply is available and the network constituting the interconnexion is simple and direct. All that is then necessary is to ensure that the phase of occurrence of the pulse and the phase of commencement of the time base, relative to the mains supply, should be constant, for the phase of this supply at sender and receiver will necessarily be almost identical. If, however, the two stations are interconnected by the mains supply, but through a major portion of the network, particularly through a number of generating stations, the phase of the supply at the two points is likely to differ considerably, according to the distribution of the load between the various generating stations.

No other common frequency suggests itself, but there is the possibility of providing one either by landline or by a separate radio channel. However, as we already have at the receiver such a common frequency in the form of the pulse, an additional source of common frequency should be unnecessary.

When a common mains supply is not available, the problem can be subdivided into the cases where the supply at the transmitter is a.-c. and where it is not; the nature of the supply at the receiver is not usually a factor to be considered. When a.-c. is available, the transmitting apparatus is simpler and more economical if the frequency of the supply is used as the recurrence-frequency of the pulse, and thus

the stability of this recurrence-frequency is at once fixed. The stability is likely to be rather poor, especially on mains supplies which do not guarantee a service for electric clocks.

The use of a stable oscillator at the receiver to control the time-base recurrence-frequency is then out of the question and something more flexible which will follow any short-period variations must be provided. This is essentially the province of a self-synchronized arrangement.

Where d.-c. power only is available at the transmitter, a local oscillator must be provided to control the recurrence-frequency of the pulse. One might use either accurately controlled oscillators at both stations with only a small amount of locking to maintain exact synchronism, or use simple control oscillators with accurate and positive locking. The former would be expensive and inflexible and it will be shown to have no particular advantage.

§ 2. THE PARTICULAR PROBLEM

A statement of the conditions for which the system was designed will assist in following the lines of development. The transmitter is located at King's College, Strand, and the receiver at the Halley Stewart Laboratory, Hampstead; the distance between the two is about 7 km. It was necessary to take continuous records of layer-height and also to make rapid determinations of the equivalent height at closely spaced frequencies; in fact as near an approach as possible to a continuous P', f curve was desired.

Both a.-c. and d.-c. power were available at the transmitter, and at the receiver there was also a.-c., but it differed in frequency from that at the transmitter and from that at the National Physical Laboratory, Teddington, the transmissions from which are much used also. Another source of trouble was the electrical interference from domestic appliances in the neighbourhood. The two disadvantages offset each other to some extent, for the disturbances do not give a stationary pattern superimposed on the echo pattern. Where such disturbances are troublesome, it is a very definite advantage if the pulse-recurrence frequency differs from that of the mains supply at the receiver.

§ 3. THE TRANSMITTING SYSTEM

The transmitter was originally operated from the d.-c. power supply, but the strength at the receiver was found to be insufficient to operate any self-synchronized scheme, so it was decided to utilize the transmitting valves (Mullard SW2B) at the voltage limit, since the dissipation is low with pulse transmissions, and at the same time to simplify the apparatus by operating entirely from the a.-c. mains. A transmitter for d.-c. operation will therefore be described, and the necessary modifications when a.-c. is to be used will be indicated.

The aerial presents the first problem since the transmitter is located on the roof of King's College and the earth below is very vague; a horizontal dipole probably offers the best solution. Much trouble might be saved by the use of a

number of aerials of different lengths connected in parallel, a plan adopted by workers in America^(a), for the coupling of the aerial to the oscillator then presents much less difficulty. Because of the wide variation of the impedance presented by the aerial for different frequencies, it is hopeless to expect reasonable efficiency from a fixed coupling, even for the range covered by one coil, unless, perhaps, a separate aerial is used for each coil. Moreover, the whole range of frequencies from 2 to 10 Mc./sec. was to be covered without a coil-change, by the use of a variometer. Variable coupling was therefore essential and capacitive coupling was the most convenient, since it can be continuously variable; such coupling also reduces the radiation of harmonics. Closely allied to this question of coupling-efficiency is that of the dependence of the length of the pulse on the load introduced into the oscillatory circuit from the aerial. If the loading is light, the time of decay of the oscillations may well be as long as 0.2 millisecond, giving a long and inefficient pulse particularly unsuitable for schemes where the transmitter and receiver are very close to each other. The aerial therefore should always be coupled as closely as possible to the oscillator, up to the point where the rate of build-up of the oscillations balances the rate of decay.

The step-down ratio required (from 25,000 to 100 Ω .) requires a large-output condenser, but an ordinary Cyldon receiving condenser of 0.001 μF ., when immersed in good transformer oil, gave the requisite capacity and withstood the radio-frequency voltages across it. This condenser is shown at C_2 figure 3. The tuning condenser C_1 is centre-pointed, with 0.0003 μF . on each side, and of the Cyldon small transmitter type.

To obviate plug-in coils, the variometer L_1 was constructed and this, in conjunction with the continuously variable output coupling used, permitted the frequency range from 2 to 9 Mc./sec. to be covered without discontinuity. Trouble was encountered in the construction of the variometer owing to the voltage step-up across either stator or rotor relative to that across the whole variometer in the minimum position. This step-up can easily be 5 to 1, and since the variometer is balanced, the stress in the insulation at the two lead-in connexions to the rotor is very high. Steatite, however, was found to be suitable as an insulating material and is easily worked.

The two halves of the tuning-condenser and the variometer are ganged but the output coupling condenser could only be included in the ganging by cutting a special cam. Shunt feed, constituted by L_2 , C_4 , is adopted for the anode supply, in order to keep dangerous voltages away from the controls and to give only radio-frequency voltages across the tuning-condensers, which are already working close to the voltage limit. The space-wound feed choke gave no trouble due to resonance effects anywhere in the frequency range. When the anode supply is alternating almost the full anode voltage comes across the tuning-condensers because the output circuit is not earthed in any way, so that it is necessary to provide two resistances R_2 of about 10,000 Ω . connecting the two sides of the output circuit to earth.

With a continuous-wave oscillator the feed-back is determined in accordance with a compromise between efficiency and power output, but for a pulse transmitter

we are concerned at this point rather with the requirement of maximum power and rate of build-up of the oscillations. For this we require considerable feed-back and it is provided by a fixed condenser C_3 of $0.0001 \mu\text{F}$. Resistances R_4 of 10Ω . connected directly in series with the grids serve to damp out spurious oscillations.

Mechanically interlocked switches S_1 , S_2 , S_3 ensure that filament, bias and anode voltages are applied in their proper order, and appropriate meters and regulating resistances are provided. A thermo-ammeter measures the current flowing in the aerial, and a switch permits the use of a 40-metre dipole or half of it as required. This switching is also effective in unbalancing the dipole sufficiently to give adequate strength to the ground ray at the receiver.

When the anode supply is alternating, it is necessary to have a capacity C_7 of about $0.1 \mu\text{F}$. across the secondary of the high-tension transformer T_3 to give the necessary steep slope to the pulse of current for the valves. This constitutes a considerable wattless load and should be balanced by a choke preferably connected across the primary of the transformer. The choke is also necessary to ensure that the phase of the anode voltage shall be independent of its amplitude.

§ 4. THE MODULATING SYSTEM

Pulse modulating systems have appeared in considerable number⁽³⁾, from the simple squegger oscillator to master-oscillator types in which modulation is effected in the amplifying valve. The criticism levelled at the simple oscillator, that the band of frequencies is excessive and erratic, does not seem to be justified in fact, and in any case with pulses of the requisite short duration the frequency band to which the measurements are to be referred is limited more by the receiver than by the transmitter. Tests at the receiver have shown that any frequency-modulation which may be present is insufficient to cause a phase-shift of the carrier of 10° in the duration of the pulse. The use of the master oscillator, then, is not justified, except for certain special investigations, in view of the accompanying expense and loss of flexibility. Another criticism of the self-excited transmitter is that it cannot easily be modulated with certainty on the grid, but the circuit to be described achieves this result positively and it is quite simple.

The value of the bias necessary to quench oscillations which have been initiated may be as high as one-quarter of the anode voltage, particularly when the drive is made very heavy to give a rapid rate of build-up. The small commercial thyatronns are rated at 1000 volts peak, forward and inverse, and since nearly twice this value can be obtained for bias purposes without exceeding the limit quoted it should be feasible to use such a thyatron for direct grid modulation for powers up to about 1 kW.

Consider the simple circuit of figure 1 (a), consisting of a choke L , a condenser C and a thyatron T connected in series across a supply circuit. Suppose the condenser to be initially uncharged and the thyatron in the non-conducting state. Then if the thyatron is tripped the condenser charges to twice the voltage of the

supply, for the low resistance of the thyatron permits an oscillatory charge. The current now tends to reverse but in so doing extinguishes the thyatron; the cycle of events is shown in figure 1 (d). Thus the voltage V_{ab} across T and C has a suitable form for the modulating bias, with peak values up to 2000 volts, and the pulse length can readily be altered by varying the product LC . The value of L/C must be so chosen as to keep the peak current through the thyatron below the limit, in this case 0.6 A., and the operation is considerably steadier if it is kept well below this figure. The voltage across the choke collapses very rapidly, in fact it oscillates with the natural frequency of the choke as shown with small dots in figure 1 (d),

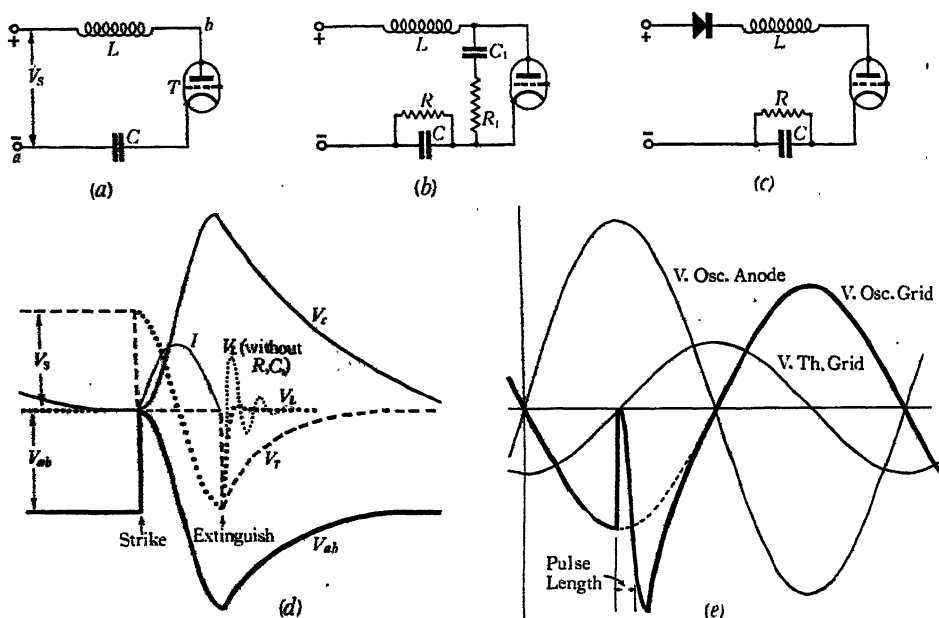


Figure 1.

so that the bias may fall nearly to zero and cause the oscillations to build up again. The simplest way out of the difficulty is to connect a condenser C_1 in series with a resistance R_1 across the thyatron as in figure 1 (b). This will have no effect while the thyatron is conducting, except to increase the peak current through it, but when it extinguishes, C discharges through the condenser C_1 and resistance and the choke, so that the voltage across the latter, shown by large dots in figure 1 (d), is no longer oscillatory. This arrangement is simple but it is not positive, and in the event of its failure the transmitter either oscillates continuously or squeggs, having to charge up the condenser across the supply circuit. When the oscillating valves are used at the voltage limit as in this case the possibility of failure cannot be entertained, for the dissipation limit is not far away even with the short pulses employed. If a rectifier is inserted in the supply lead before the choke, as in figure 1 (c), then any grid current or any charge on the grid must be diverted into

the condenser C , and if the oscillations are not fully quenched this condenser becomes the reservoir condenser of a squegging circuit and the oscillations must be quenched by the squegging. If this rectifier is of the gas-discharge type it will not appreciably affect the oscillatory nature of the charge of C , and the pulse length is controlled entirely by the modulating circuit. If a thermionic rectifier is used the arrangement gives a compromise between the above conditions and a positively-controlled squegging oscillator.

To ensure that the condenser C is completely discharged just before the beginning of the pulse it is necessary to connect a leak R , figures 1(b) and 1(c), across it, and the limits of the time constant of this combination depend on the nature of the supply to the anodes of the oscillating valves. If the supply is a.-c., then the holding bias also can conveniently be alternating voltage of suitable magnitude and 180° out of phase with it. The thyatron is tripped when the anode voltage is at its maximum positive value, again by an alternating voltage which leads the thyatron anode-voltage by 90° . The time constant RC must then be not less than one-quarter of a cycle, corresponding to a time of 5 msec. for a frequency of 50 c./sec.; it must also be well below 10 msec., otherwise the condenser will not be fully discharged by the time the next pulse is due to occur. The range of values is quite limited and care must be taken to ensure that it shall not vary beyond this range with variation of the humidity, etc. Figure 1(e) shows the cycle of events in a system operated entirely by the a.-c. mains supply.

With d.-c. supply to the anodes of the oscillating valves, the holding bias must be maintained except for the short time during which the pulse is being generated, and the voltage across the thyatron must be maintained over the same period, for, though it is negative at the moment of quenching of the oscillations, it returns fairly rapidly to positive values. The tripping pulse for the thyatron must be quite short, of the order of 1 msec., and this figure is then the lower limit for the required time constant. The range of values in this case is much less restricted.

A convenient circuit for obtaining the tripping pulse for the thyatron is shown in figure 2. An a.-c. voltage of about 100 is applied through the primary of a transformer to the anode of a valve of the small-output type used in receivers, and to the grid of this valve is applied an a.-c. bias, leading the anode voltage by nearly 90° , from the network L, R, C , as shown. When the grid becomes negative, the sudden stoppage of anode current causes the voltage across the transformer to rise, and the voltage across the secondary, together with the necessary steady bias, is applied to the thyatron grid. This scheme gives a pulse of duration 0.5 msec., in shape approximately half of a sine wave, and seems preferable to the usual devices for deforming wave-form, with which the point of tripping is likely to be erratic. The primary inductance and self-inductance of the transformer should be kept low and the external circuit of the secondary should be purely resistive, or the pulse will be unduly lengthened. A resistance is connected in series with the grid of the thyatron to limit the current when the arc strikes.

A suitable modulating bias having been obtained, it has to be applied in the most efficient manner to the grids of the oscillating valves. In the complete

schematic diagram of the transmitter, figure 3, it is seen that the steady bias reaches the grids through the resistances R_3 . If a short pulse is applied to the grids through these, it will be considerably distorted and the voltage on the grid will fall relatively slowly. Now the time taken for the oscillations to build up to a given value depends on the initial disturbance, or on that part of the disturbance which occurs in the first half-cycle of the oscillation. It is therefore necessary to apply the steep initial portion of the modulating pulse to the grids in the shortest possible time. This involves the provision of a capacitive path as well as the resistive one; a condenser across R_3 would short-circuit the radio frequency drive on the grids, but the connexion of the centre point of the tuning-condensers C_1 to the centre point of the resistances R_3 provides the required capacitive path, if the bias is applied between this point and the filaments. The impulsive kick on the grids can be regarded as a sharing of charge between the grid-filament capacities and the other capacities in series, and, with the values in use, it is found that only about three-quarters of the full amplitude of the impulse gets on to the grid immediately, and that this may still not be enough to bring the bias to the point where the oscillations build up at the maximum rate, i.e. to the straight portion of the grid-volts, anode-current characteristic of the valve. It is necessary then to bring the connexion from the filaments to a potentiometer connected across the terminals which supply the modulator circuit, and to provide a capacitive path across one side of this, which accounts for R_3 , R_9 and C_9 .

§ 5. THE RECEIVING SYSTEM

The pulses are received on an inverted-L aerial with a long horizontal portion and only enough down-lead to give the requisite strength to the reception of the ground-ray. This aerial is coupled to a receiver of the type designed by Dr G. Builder for this type of work⁽⁴⁾. The output from the linear detector is fed direct to one pair of plates of the cathode-ray oscillograph, with the time-base on the other pair, and the lay-out is arranged for visual observation and for photographic recording.

§ 6. THE SYNCHRONIZATION PROBLEM

Preliminary considerations of the possibilities and requirements of a locking arrangement for use in this work have already been indicated. The first scheme which occurs to mind is to have extremely stable oscillators controlling the recurrence-frequencies of pulse and time-base. In this case we can be sure that the difference in frequency between the two oscillators will never be large and we can make the locking effect very slight, so that random disturbances will not affect the frequency or phase of the controlled oscillator to any great extent. If the locking effect is small, however, considerable phase-variation between the two oscillators is possible for small variations in the natural frequencies, and this will cause the trace of the ground-ray to wander in position along the time base; but

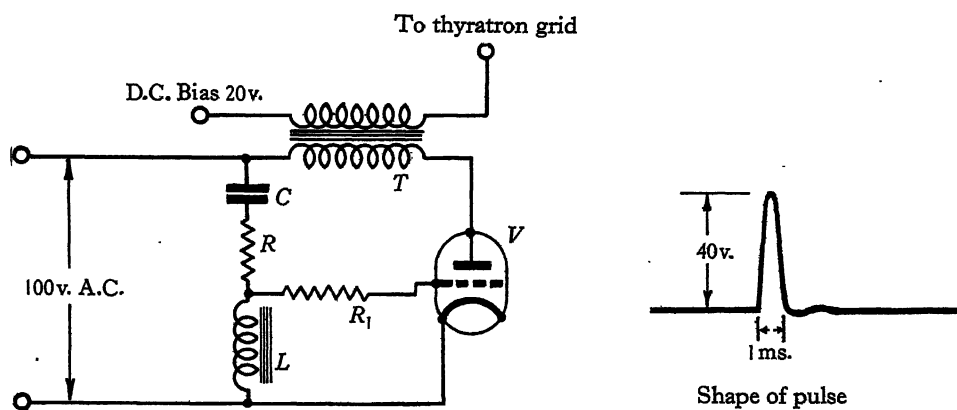


Figure 2. Circuit producing short d.-c. pulses.

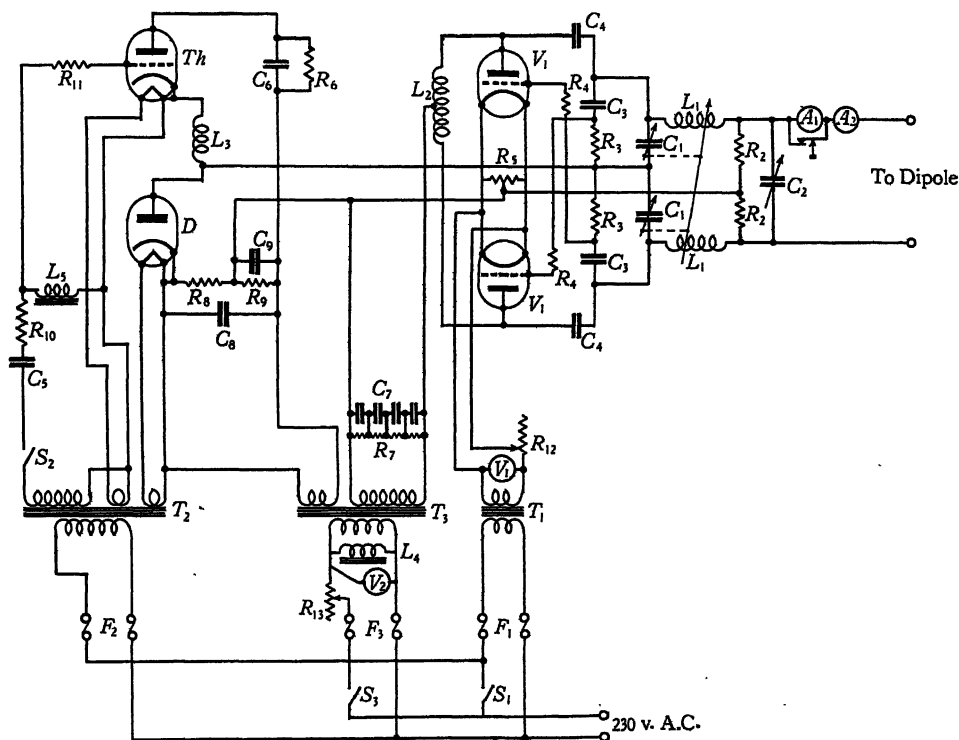


Figure 3. Radio-frequency pulse-transmitter.

the necessary compromise still retains the feature of insensitivity to random disturbances. The use of two such oscillators would be expensive and will be shown, after comparison with other schemes, to have negligible advantage for the purposes in view.

Another case arises when the recurrence-frequency of the pulse is, of necessity, rather variable, for instance when it is controlled from the a.-c. mains. At the receiver we must have a control oscillator which can be made to follow these variations. It is impracticable to adjust the natural frequency of the time-base control oscillator by means of the received pulse, but it is possible to adjust its phase, or to speed it up during a portion of its cycle. We should prefer to start the time base just a little before the arrival of the ground signal, so that we could observe and measure from the beginning of the pulse. But since the pulse itself has to provide, even if indirectly, the necessary speeding up or phase-adjustment of the control oscillator, the phase of the point in the local cycle of events just before the arrival of the pulse, relative to the phase of occurrence of the pulse in the cycle of events at the transmitter, will vary as the frequency varies. Thus a continuous record of the layer-height is likely to show considerable variations of the base line (the ground-ray trace) and this would make the interpretations of heights more difficult and the variations thereof much less obvious.

The only way out of this difficulty is to make the arrival of the pulse the beginning of the cycle of events at the receiver, in other words to make the pulse start the time base on its sweep. This entails the loss of a portion of the beginning of the pulse and we are left with some uncertainty in the measurement of heights. But since the apparatus will lock satisfactorily with a pulse-amplitude only one-tenth of that normally used, and since the duration of the upstroke is only about 0.1 msec., the error in time is not greater than 0.01 msec. plus the time taken for the time base to start on its sweep, which is not more than 0.01 msec. Now 0.02 msec. corresponds to a height of 3 km., which is of the order of accuracy in measurement under any circumstances. With this arrangement the pulse always occurs at the beginning of the time base and so gives a straight line on continuous records. If the above error cannot be tolerated, then we are forced to use the previous scheme and to put up with the uncertain position of the ground pulse; this uncertainty in turn introduces its own errors, unless the time scale is very uniform or the calibrating marks are very close.

The next point for consideration is the interference due to random disturbances, to which is closely allied the tendency to lock on echoes rather than on the ground pulse. This latter effect is discussed elsewhere⁽⁵⁾, and a circuit is given for overcoming the difficulty; but it can be overcome more simply by the use of a thyatron, as will be shown later. The following discussion is not concerned with the actual procedure adopted. The first echo to be received may, on occasion, be as much as 4 msec. later than the ground pulse; it may be extremely wide, and never fade completely to zero. If by chance this late echo should be in a position to cause locking, the ground ray must be capable of regaining control, or long periods of the record will be valueless. If we cater for this eventuality, then, when the time

base is correctly locked on the ground pulse, any disturbance occurring 4 msec. before is capable of taking control. If the ground pulse is not above the general noise level the position is hopeless, for discrimination between random disturbances and the recurrent pulse over a period of 4 msec. is impossible.

Normally there are echoes of much less delay and, though an individual echo may be as much as 10 msec. later than the ground ray, echoes before it will successively take control until the ground pulse is able to do so. If an observer is present he can take care, by manual control, of the relatively rare contingency discussed above, but for purely automatic recording of the critical conditions of the Appleton region it is preferable to design on the basis of this figure of 4 msec. for the delay of the first echo. Even in a scheme using extremely stable oscillators for control purposes at transmitter and receiver, opportunity to lock on an echo is sure to be given when atmospherics are bad, and if the scheme is designed on the basis of the above figure, it loses its main advantage, i.e., its discrimination against random disturbances.

The displacement of the pattern due to a disturbance prompts an investigation of the time efficiency of the system, i.e., the proportion of the total time during which the pattern is in its correct position. A scheme giving the greatest time efficiency over short periods does not necessarily give the best efficiency over long periods, but it gives at least as much information so that short-time efficiency must be the criterion. In the type of P', f records taken in this laboratory a period as short as 15 sec. is allowed at each frequency and at least 5 sec. of this must be allotted to changing of frequency and retuning. If therefore the pattern should be displaced, it must take up its correct position in much less than 10 sec., preferably in less than 1 sec.; the lower limit is 0.1 sec., set by the 4 msec. over which the pulse must be effective in locking. In actual practice, the figure can be made as low as 0.2 sec., and no manual control could bring it into position as quickly as this. Even for a value of 0.5 sec., the difference in natural frequencies of the two control oscillators becomes 2 c./sec., when frequency-variations as great as 1 per cent become negligible. This consideration nullifies the advantages of the stable oscillator scheme.

§ 7. THE SYNCHRONIZING SYSTEM

With the general considerations outlined above in mind, the arrangement shown in figure 4 was devised. A tuned circuit L, C is maintained in oscillation by the valve V_1 at a frequency of about 50 c./sec.; a certain amount of drive is also derived from the anode circuit of the thyatron V_3 , as is apparent from the diagram. The amount of this drive is controlled from the pulse itself, the oscillator being thus synchronized with the recurrence frequency of the pulse. A portion of the oscillatory e.m.f. is applied to the grid of the valve V_2 , which then acts as a switch for the thyatron. It has been found quite feasible to effect the extinction of the thyatron arc by grid voltages of the order of one-quarter of the anode voltage, for currents through the thyatron up to 50 mA., provided that the voltage on the

anode cannot rise when extinction occurs. The thyatron thus regains some of the advantage of the thermionic valve, in that both the conducting and the non-conducting states can be controlled by the grid.

By a suitable choice of the resistance-capacity circuit R_2, C_2, R_{12} , in the anode circuit of V_2 , a voltage cycle of square form is obtained across R_2 when a sine wave is impressed on the grid, and this is capable of tripping and extinguishing the thyatron at the appropriate instants. The inductive load L in the thyatron anode circuit would give a rise in voltage at extinction, but this rise is limited by the resistance-capacity circuit R_3, C_3 , across the thyatron (whose primary function, however, is to switch the time base) and also any rise of voltage across the induc-

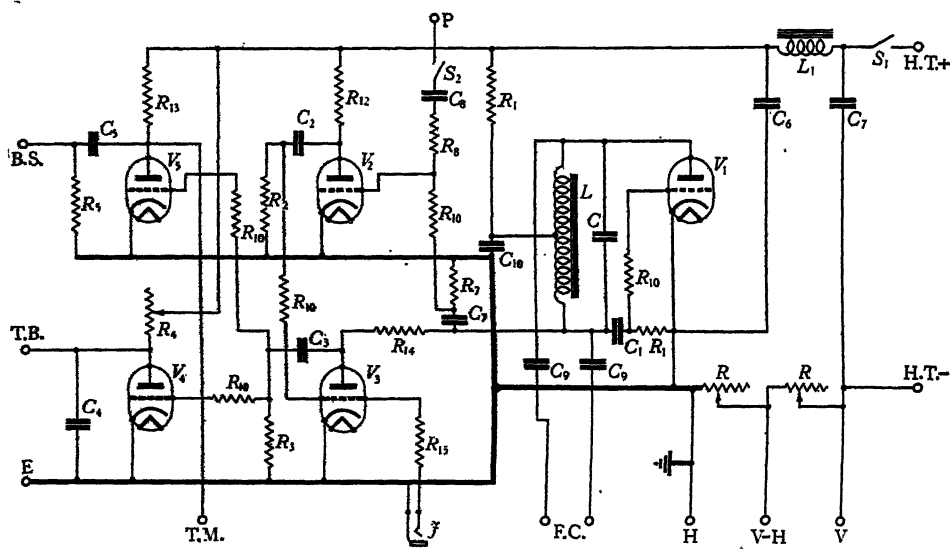


Figure 4. Pulse-synchronized time-base circuit.

tance would cause the other valve V_1 of the push-pull circuit to become conducting, so that it is doubly safe-guarded. The negative pulse from the receiver is also impressed on the grid of V_2 through the terminal P , and if it occurs before the grid has acquired a negative charge under the influence of the control sine wave from the oscillator, it causes the thyatron to strike sooner than usual and the oscillator is speeded up. Should the pulse occur too soon, so that the grid of V_2 goes positive again under the influence of the control voltage, the thyatron is duly extinguished but the locking effect is so considerable that the oscillator is speeded up till the pulse is in the correct position. A disturbance occurring at such an early stage merely registers as a gratuitous ground pulse, but does not affect the time scale because the condenser of the time-base circuit discharges almost immediately on the extinction of the thyatron and conditions are always the same (the condenser is always discharged) at the beginning of the time base proper. The

direct induction into the receiver from the thyatron is not serious, except occasionally when the latter is near the end of its life.

The resistance-capacity circuit R_3 , C_3 across the anode circuit of the thyatron gives a voltage cycle across R_3 of much squarer wave-form than that across R_1 , and this voltage controls the time base. The time base valve V_4 , then, is conducting, and the condenser C_4 is discharged, till the thyatron strikes; when the pulse arrives and trips the thyatron, all anode current through the valve V_4 is cut off and C_4 charges through the resistance R_4 . The voltage across C_4 is taken to one pair of plates of the oscillograph and constitutes the time base. Thus the pulse always occurs at the beginning of the time base and it has been shown that the portion not registered is of the same order as the accuracy of measurement. It should be noted that the amplitude of the pulse necessary to trip the thyatron depends on the amplitude of the control voltage on the grid of V_2 , and on the difference between the natural frequencies of the control oscillators at the transmitter and the receiver or the tightness of locking. The portion of the pulse lost as a result of the use of this system depends on the above two factors and also on the steepness of rise of the pulse. The estimated value of 10 μ sec. for the time lost in actual operating-conditions is readily attainable.

The valve V_5 is controlled in like manner to V_4 from the resistance R_3 , but the resistance-capacity connexion R_5 , C_5 , R_{13} in the anode circuit is so chosen as to give a square wave-form across R_5 . This voltage is applied to one of the other pairs of plates of the oscillograph, so that the backstroke of the time base is deflected in the opposite direction to the pulse and is therefore removed from the field of the camera. Two pairs of coils on a suitable core of transformer-steel stampings are connected in the high tension negative lead to the unit, with a variable resistance R across each pair, to provide a ready means of adjusting the time base both vertically and horizontally. This arrangement eliminates origin-distortion in the oscillograph.

An exponential time base has been used for the sake of simplicity and because it gives a greater range of heights for a given accuracy of the lowest height. It can be taken as uniform over 100 km. and, since marks for every 50 km. appear on every photograph, non-linearity is no drawback.

The frequency of the local control oscillator, and thus indirectly the amount of locking, is controlled by a variable resistance (connected externally to the terminals F.C., and placed in the manner convenient for the operator) in series with the condensers C_8 , connected across the oscillatory circuit. This method of control introduces a variable load into the oscillating circuit but is more convenient than a variable condenser, which would have to be inconveniently large.

If at any time it should be requisite to have the whole of the pulse on the time base, e.g. when maximum accuracy in height-measurement is essential, it is only necessary to control V_4 and V_5 from the oscillatory circuit, so that the voltage is slightly dephased, in order to start the time base before the arrival of the pulse. The locking process functions as before and there is no distortion of the time scale, but any variation of the recurrence-frequency of the pulse will cause the

ground-ray to wander in position, as has been pointed out above. The amount of locking and the degree of discrimination between pulse and disturbance are fixed by a suitable choice of R_{14} , R_{10} and R_8 .

Since no steady bias is used, from considerations of simplicity and economy, the phase of striking of the thyatron is considerably later than that of zero e.m.f. in the oscillatory circuit, although this point would give the optimum locking effect. The voltage on the grid of V_2 is advanced in phase by the resistance-capacity combination R_7 , C_7 to compensate for this defect.

Resistances of the order of 250,000 Ω . are inserted in series with all grids to limit the flow of grid current when such high positive biases are used. A short-grid-base valve such as the MH_4 type is used for the control valve, since it gives a sharper wave-form in the anode circuit for a given grid voltage, and the small power type (AC/P) is used for V_4 and V_5 , where the d.-c. resistance is the important factor.

The unit is run entirely from the a.-c. mains supply and, since the local control frequency is only slightly different from the local supply frequency, the smoothing in the eliminator circuit must be considerably more efficient than is usual. In this connexion it may also be mentioned that the commercial type of high-tension supply units for cathode-ray oscillographs require additional smoothing.

§ 8. CALIBRATION OF THE TIME BASE

A calibration of the time base is necessary, and the usual procedure is to photograph at intervals the output from an oscillator, which is deformed if preferred and is applied to the oscillograph in place of the echo pattern. With an exponential time base it is preferable to make the reference points as numerous as possible, so that a frequency of 3000 c./sec. is suitable, for then each complete cycle represents 100 km. of path or 50 km. of height. This calibrating oscillator is usually locked to a harmonic of the time-base recurrence-frequency, but, as was mentioned above when the locking of the control oscillator to the pulse recurrence-frequency was being considered, there must be some phase-variation between the two oscillators, so that the markings bear no fixed relation to the beginning of the pulse, and this point is not available for measurement in the scheme outlined above. The difficulty is eliminated if one of the time marks is made coincident with the arrival of the pulse or the beginning of the time base; this requires that the condition in the calibrating oscillator shall always be the same at the beginning of each time-base sweep, and the simplest and most reliable condition is that of quiescence. Then the oscillations should be started by some event coincident with the beginning of the time base, attain a reasonable amplitude in as short a time as possible, and maintain it for the duration of the time base.

The voltage on the grid of the thyatron is of a suitable form for controlling such an oscillator in that it is very negative before the commencement of the time-base sweep and practically zero during it. The grid of the oscillating valve V_1 ,

figure 5, is therefore connected (by a jack lead) to that of the thyatron through a resistance R_{15} , figure 4, of about $250,000 \Omega$., and another similar resistance R_1 , figure 5, is connected from the grid of V_1 to its oscillatory circuit. This arrangement is found to be very satisfactory, the oscillator attaining its maximum amplitude in about 5 cycles and decaying completely in about 5 msec.

Since this time-marking will always be fixed in position relative to the beginning of the ground pulse, it can advantageously be superimposed permanently, provided that the echo pattern is not unduly distorted in consequence. Two stages of wave-form deformation are required, as shown in figure 5; the full oscillatory voltage is applied to the grid of V_2 through the limiting resistance R_6 , and a very peaked wave-form is obtained across R_3 by suitably adjusting the values of R_5 , C_3 and R_3 ,

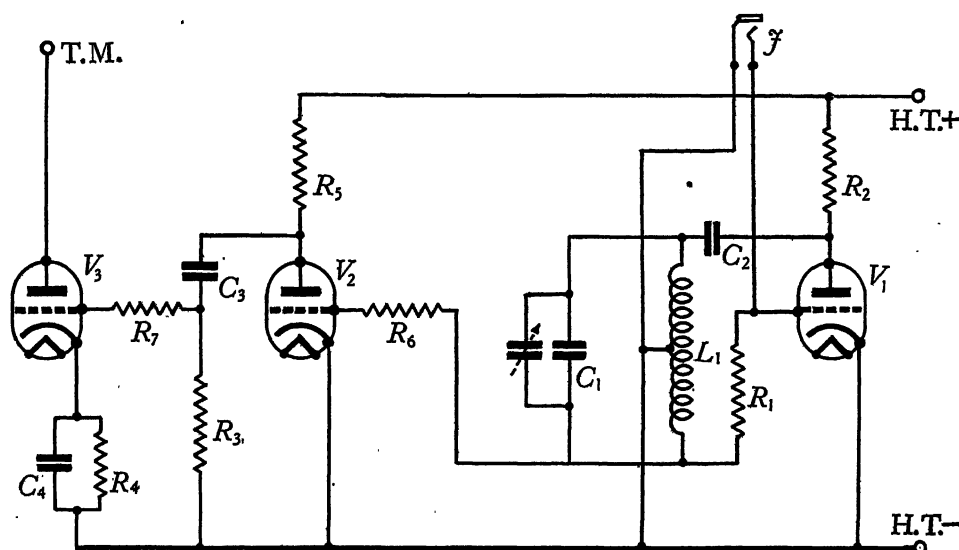


Figure 5. Calibrating oscillator.

in the anode circuit. The voltage across R_3 is applied to the grid of V_3 , and the biasing circuit R_4 , C_4 , in the cathode lead, ensures that current shall pass for a very short period only. The anode of this valve is connected in parallel with that of the valve V_5 in figure 4, through the terminal T.M., so that the oscillograph spot is deflected momentarily to the backstroke position and the time base appears as a discontinuous line.

Careful check observations, made by applying the output from a separate stable oscillator to the oscillograph in place of the echo pattern, and also by comparison of the heights of second and third order reflections, show that the equivalent height at any point as indicated by this method is in error by not more than 2 km. for heights from 100 to 1000 km., i.e., the accuracy attainable is of the order of the accuracy of measurement, when the readings are adjusted to be correct at the limits given. The 50-km. mark is unreliable because of the smallness of the ampli-

tude of the oscillation at this point, but this is of no moment since echoes rarely appear below an equivalent height of 100 km.

The advantages of the scheme are numerous. Heights can be read off at once and the variations of height are immediately obvious, even if the time base alters its position in the camera field. The time scale can be varied without any necessity for a separate calibration, and any variations are automatically checked. A portion only of the time base need be kept under observation if required, without loss of accuracy. Finally, since the oscillator is not locked to a harmonic of the time-base frequency, variations of the latter can cause no error. But illustrations of the operation will give the best idea of its suitability for this type of work under the conditions imposed.

§ 9. RESULTS

In figure 6 are shown two records of the kind taken daily at the Halley Stewart Laboratory, showing the variation of the equivalent height with frequency. The frequency at the transmitter is changed by approximately 0.3 Mc./sec. every 20 or 30 sec.; at present this is still done manually, from 2 to 3 sec. being required for the change. At the receiver, the echo pattern is screened off except for a strip 1 mm. wide along the base line, so that the echoes appear as a missing part of the time base, and, when photographed, the trace appears white on a black background⁽⁶⁾. During the retuning period the echo pattern is absent, and so a continuous black line across the record, which serves to distinguish one frequency from the next, appears. The frequency steps have been calibrated so that the frequency of each section is known, the sections being identified by means of a suitable scale. The photographic paper is moved through the camera at a speed of 2 ft. per minute by means of a small gramophone motor of the induction type, the speed of which is reasonably constant. The time required at the receiver for retuning is about 2 sec. so that a period of 15 sec. is available for recording at each frequency, and this is long enough to ensure a fair sampling of conditions. These figures permit us to cover the range 2.4 to 6.0 Mc./sec. in half an hour; the time spent on each frequency can be reduced to 15 sec., but this leaves no margin for accidents, and it is unwise to lengthen the time, for temporal variations in height may be considerable.

The amount of detail available in these records is at once obvious, and it is usually possible to identify the critical frequencies of both the ordinary and the extraordinary rays for all the reflecting regions, of which as many as five components appear on some records.

In the upper record in figure 6 the ordinary ray first appears in the lower *E* region (*E*^I) at a height of 120 km., rising suddenly to the intermediate region (*E*^{II}) at 140 km., later passing to the *F* region at 210 km. and finally penetrating this also. The nomenclature adopted for the various regions is that suggested by E. V. Appleton⁽⁷⁾. The extraordinary ray follows the same procedure, but always makes the jump at a higher frequency, the actual value of the separation being about 0.7 Mc./sec. for each of the three regions, indicating that electrons are pre-

dominant over ions in all regions. The vast majority of records show this normal separation for all regions, but the lower record of figure 6 shows a definite departure from the value of 0.7 Mc./sec. For the ordinary ray, there is a trace of reflection from an intermediate region and then the obvious jump to the *F* region which it penetrates in the usual way. The extraordinary ray, however, appears to penetrate the *E* region about 1.4 Mc./sec. later than the ordinary ray, though it penetrates the *F* region with the normal separation. A multiplicity of echoes is to be noted just after the ordinary ray has penetrated the lower layer; it is possible to distinguish the first, second and third reflections coming from region *E*, and the

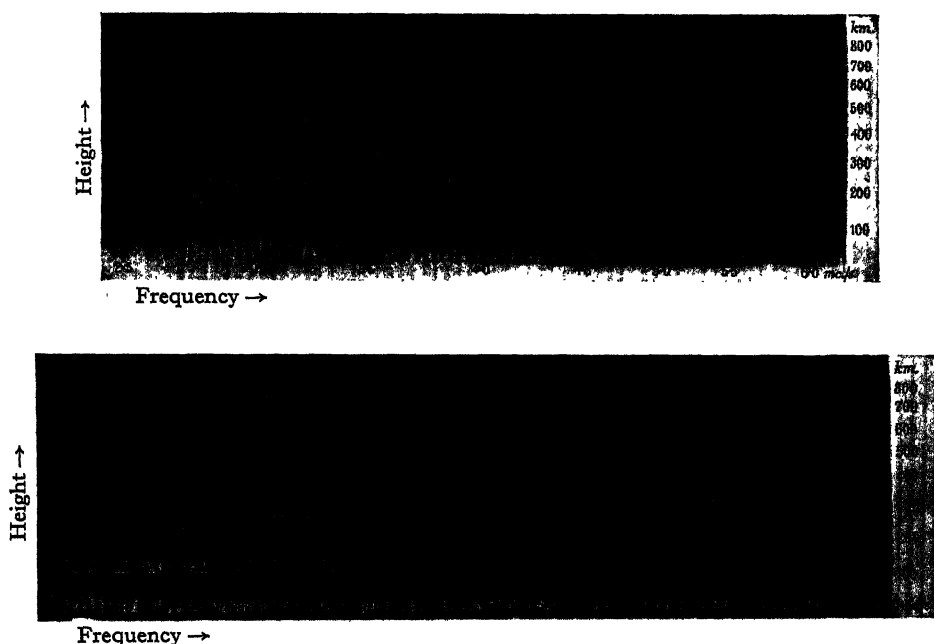


Figure 6.

first and second coming from *F*, together with another echo which must be interpreted as the *M* reflection postulated by Ratcliffe and White⁽⁸⁾, i.e., a ray reflected twice from the *F* region and once from the upper surface of the *E* layer. This type of reflection is commonly associated with the delayed critical frequency of the *E* region as illustrated in this record.

In the lower record of figure 7 is an example of a *P', t* trace, wherein the frequency of the transmitter is fixed and the paper in the camera is moved continuously, so that the variation of the equivalent height with time is recorded. The height-calibrations are very well reproduced in this record, the distance between each of the fine horizontal white lines being equivalent to 100 km. in path or 50 km. in height. The extraordinary ray is to be seen at a height of 300 km. and the ordinary ray varying from 350 km. upwards; this component itself splits into separate components, and on occasion these can be observed to cross and

recross each other, as indeed they appear to do in this record. The beginning of the ground pulse does not reproduce very well on the photographs, but in the originals it can be distinguished as a fine black line at the lower edge of the record.

The upper photograph is a record taken when no ground-ray was present; it will be seen that we can get the equivalent heights from the distance between the first and second reflections, and from these data the height of the other component can be deduced. Though these records have been taken under conditions which are probably better than normal, it is possible to follow in the originals the traces of echoes even when the disturbances are so bad that the signal is not distinguishable by ear from the general noise.

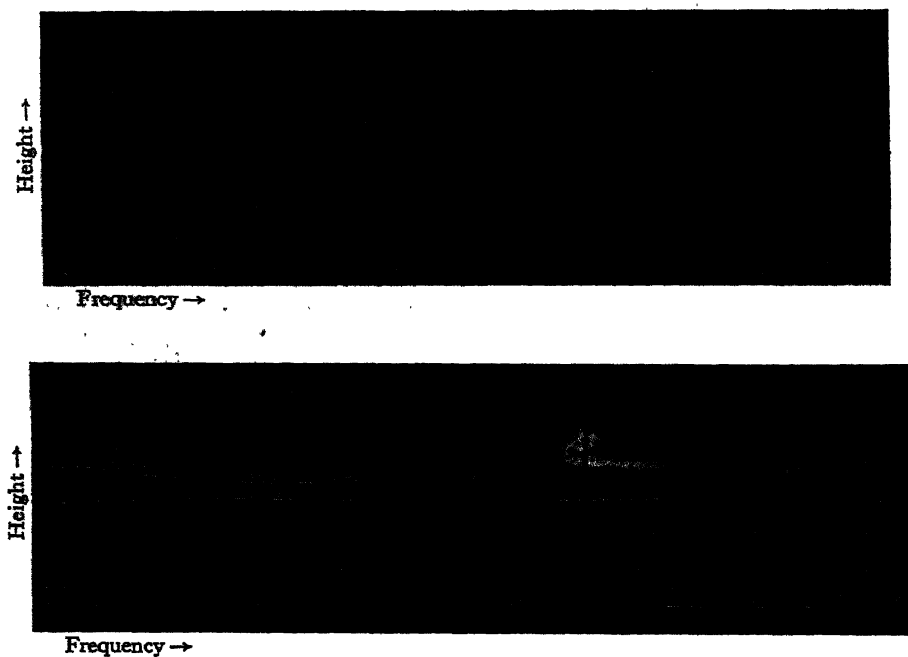


Figure 7.

§ 10. CONCLUSION

It has been demonstrated that, even when there is no common control frequency available at both transmitter and receiver, it is quite feasible to obtain records containing almost as much information as under the very best conditions, the sole proviso being that the ground signal must always be somewhat above the general noise-level. A very definite advantage is conferred in those cases where the disturbances are due to such causes as domestic appliances run from the local mains supply, when they may occupy almost the whole of the cycle, for no amount of phase-shifting can then keep them off the echo pattern.

§ 10. ACKNOWLEDGMENTS

The work described in this paper was carried out as part of the programme of the Radio Research Board of the Department of Scientific and Industrial Research. I wish to express my indebtedness to Prof. E. V. Appleton for initiating and providing for the construction of the apparatus, and for his continued help given by way of suggestion and criticism; to Dr G. Builder who evoked many helpful discussions while engaged on similar problems; to Dr E. G. Bowen, for a number of suggestions; and finally to Messrs Lordon and Roberts, for help in operating the transmitter and receiver respectively.

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THE MAGNETIC SUSCEPTIBILITIES OF THE ANHYDROUS AND HYDRATED SULPHATES AND DOUBLE SULPHATES OF THE MAGNETIC METALS: WITH A NOTE ON THE INCREASED SUSCEPTIBILITY PRODUCED BY HEATING COBALT SALTS

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ABSTRACT. It has been recognized for many years that the molecular susceptibility of many salts, particularly sulphates, is greater in the hydrated than in the anhydrous condition. Measurements of susceptibility for anhydrous and hydrated single and double salts have shown that the increase is not a specific property of water but that when potassium or ammonium sulphate is substituted for the "water of constitution" there is an increase in molecular susceptibility. With the sulphates of iron, cobalt and nickel this increase is greater than that due to a molecule of water. With manganese sulphate the difference is small but in the same direction, but with copper sulphate a molecule of water increases the susceptibility to a greater extent than a molecule of potassium or ammonium sulphate.

Note relating to the increase in susceptibility of cobalt salts after being strongly heated. The effects observed by A. Serres and by A. Chatillon have been examined and an increase in susceptibility after heating has been found, but in certain salts this is complicated by the fact that hydrolysis or oxidation occurs with the production of basic salts or oxychlorides which also cause an increase in susceptibility. Cobalt pyrophosphate appears to be stable when heated in air to 600° C. and exhibits an increase in susceptibility free from complications.

§ 1. INTRODUCTION

WHEN Wiedemann about 70 years ago put forward his additive law, he quite clearly recognized that chemical changes may entirely alter the magnetic properties of substances. He was the first to mention* that a magnetic compound could be produced from two diamagnetic elements, copper and bromine. He also specially drew attention to the fact that the atomic magnetism of hydrated oxides and salts is, in general, greater than that of the corresponding anhydrous substances.

He stated that the magnetic properties of cobalt and nickel cyanides disappear when these bodies are dissolved in potassium cyanide, and concluded that this would not have happened if they had merely formed double salts.

* *Comptes Rendus*. 67, 833 (1868) from *Monatsberichte d. Königl. Preuss. Akad.* July 1868.

Mlle E. Feytis* appears to have been the first investigator to measure in modern units the susceptibilities of hydrated and anhydrous copper sulphate and came to the conclusion that the molecule of water of constitution increased the susceptibility, while the four additional molecules in $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ were merely additive and behaved diamagnetically. F. W. Gray and W. M. Birse† came to a similar conclusion in regard to copper sulphate, saying that the first molecule of water increased susceptibility by 11.5 per cent, while the further addition had no marked effect.

As Graham had shown about a century ago that in salts of that kind the water of constitution could be replaced by the neutral sulphate of an alkali metal, it appeared of interest to determine whether, for example, when potassium sulphate is left in combination with a sulphate of one of the magnetic metals the susceptibility is that of the anhydrous salt or whether it is increased in a manner analogous to the effect of water of constitution.

§ 2. APPARATUS

Two modified forms of the Curie balance have been employed; the first and older balance had a thin phosphor-bronze suspension 15 cm. in length, and the observation was made by directly reading the number of degrees turned through by the torsion head in order to pull the specimen out of the gap between the poles of the fixed magnet. It was furnished with two permanent magnets of different strengths and an electro-magnet, any of which might be used, and in this way it covered a very wide range of susceptibility when the field was varied. But the rotation was difficult to read much more closely than to half a degree, so that with small deflections the accuracy was not very great.

Instead of this direct-reading instrument a reflecting one has been employed somewhat like the Curie-Cheneveau‡ balance but with a differently shaped magnet which is caused to slide along brass rails by means of a long brass screw having 20 threads to the inch. The arrangement used by Cheneveau, in which the magnet is moved in an arc concentric with the suspension of the radial arm, has not been followed. I freely admit that this arrangement has the great advantage of keeping the specimen in the centre of the gap even when large deflections are used, but the method of rotating the magnet by means of an arm or yoke with tiller lines or reins as described by Cheneveau did not seem to possess the requisite mechanical exactitude or delicacy. The application of gearing that would be free from back-lash and at the same time not excessively slow presents a difficulty, but not an insuperable one. This principle seems to possess great advantages and if the present instrument were reconstructed a circular motion would be adopted.

The drawback due to the relative shift of the specimen along the y -axis with the rectilinear motion of the magnet along the x -axis is partly met in the present instrument by the wide pole-gap (16 mm.) relative to the diameter of the specimen tubes (8 mm.) and by the small angular displacement of the balance arm, which is not more than 6° on either side of the zero position and frequently much less.

* *Comptes Rendus*, 153, 668-71 (1911).

† *J. Chem. Soc.* 105, 2707 (1914).

‡ *Proc. Phys. Soc.* 22, 343-59 (1910).

In the instrument described by E. Wilson* the straight-screw method was used, but in that case an electromagnet was employed: where a battery of large accumulators is available and the current can be regulated by large resistance frames, such as are met with in an electrical engineering laboratory, the variation in the resistance of the copper coil of the magnet due to heating may become negligible; but even then the current has to be very accurately read, for its value must be squared since the pull varies as H^2 . Also the change in the reluctance of the iron core and pole-pieces for different excitations must be taken into account by plotting a calibration curve for H . Thus the constancy of a permanent magnet as used in the Curie-Cheneveau balance has much to recommend it.

The magnet used in the present instrument was last magnetized 12 years ago, so it may be considered to have reached a steady state. Its poles are 5 cm. deep, slightly coned, and the flat opposed faces are 12.5 mm. wide and 16 mm. apart. The strength of field in the centre of the pole-gap was measured and found to be 530 c.g.s. units; actually in the position in which the pull on the specimen is a maximum, the value of H is somewhat less than 500, but for comparative purposes the field-strength may be taken to be about 500 units.

Thin-walled soda-glass tubing of external diameter 8 mm. was used for containing the specimens throughout all these measurements. The glass was found to be diamagnetic, with a very small negative susceptibility of approximately -0.06×10^{-6} , a value so small that when the strong suspension was used no deflection could be read and with the weak suspension the double deflection was only 3 mm. on a scale at a distance of 1 metre. These suspensions were of phosphor-bronze strip 0.85 mm. wide and the weaker one gave 6.8 times the sensitivity of the strong one.

So long as the quantity of substance occupied from 2 to 4 cm. of the length of the tube the force was found to be proportional to the mass, but any length greater than 4 cm. showed a slight diminution due to the fringing of the magnetic field near the top and bottom of the magnet poles. It will be seen that with a substance occupying 4 cm. there was 0.5 cm. between the top and bottom of the specimen and the limits of the magnet poles, 5 cm. deep.

§ 3. SOURCES OF ERROR

The most common source of error in the use of magnetic balances of this type appears to lie in the use of specimens or containers of different diameter: as $H_y \cdot dH_y/dx$ has a maximum over a very narrow belt on each side of the magnet poles, any appreciable increase in diameter must necessarily cause some part of the section of the specimen to lie in a part of the field which is farther from the zone of maximum force, with the result that lower readings for susceptibility with larger diameters are inevitable. Any substance with a susceptibility so great that it materially alters the distribution of the lines in the field is obviously unsuitable for measurement with this form of instrument. The scale, which was divided into millimetres, was bent into a curve of radius 1 m. and situated 1 m. away from the mirror attached to the

* *Proc. R. S. A.*, 26, 429-55 (1918).

bar carrying the specimen. The mirror was concave of focal length 1 m., and a collimating lens was used in front of the narrow slit. The position of the edge of the image could easily be read to 0.5 mm., or even more closely, but the deflections on repetition were rarely more constant than to 1 mm. though they could be relied upon to that extent.

On a deflection of 300 mm., the error would not be greater than 1 in 300. The results for the mass susceptibility are therefore usually given to only 3 significant figures, but when a mean of several readings has been taken a second place of decimals is sometimes given though without any claim to great accuracy. When the weak suspension is used the results are shifted nearly 10-fold but the fourth figure, when given, is still doubtful.

The arm carrying the specimen was of aluminium and counterpoise weights were arranged so that they could slide along the arm on the side opposite the specimen. This arm was fully 2 cm. above the magnets when the strong suspension was used and 3 cm. when the weak one was used: no deflection due to the arm alone was observed.

There was however a small possible error worth recording, due to the fact that when not in use the magnet had a soft-iron armature placed across its poles; when this had been in position for a day or more, on its removal the instrument gave with a standard specimen a slightly greater deflection than normal, but after about half an hour the deflection was found to have recovered its usual value after which it remained constant for many hours. Even an aged magnet may have its magnetic flux temporarily increased by the use of an armature.

§ 4. SPECIMENS AND RESULTS

The salts used were of a high degree of purity, generally recrystallised, and nearly all the double salts were specially prepared for this research. The water of hydration was checked by weighing before and after dehydration. The latter process, in certain cases, was carried out in a current of dried carbon dioxide to prevent oxidation and in certain cases in a vacuum to prevent access of oxygen and also to remove the water vapour as quickly as possible. Details are given later.

All the salts of manganese, iron and cobalt and many of those of nickel and chromium were measured with the strong suspension, but some of the latter and all the copper salts were measured with the weak suspension to obtain the necessary sensitivity.

The susceptibility employed as a standard does not depend on the selection of some particular salt, but partly upon the absolute constant for the instrument found by my old friend and colleague the late Prof. Ernest Wilson in the paper already referred to. It also depends upon tests carried out with this and another instrument* devised by him. Various specimens were measured by both of us, in my case with a reflecting magnetometer and also with the balance first mentioned in this paper. In this way an average constant and standard of susceptibility were arrived at.

* *Proc. R. S. A.*, 98, 274-84 (1920).

As one of the chief objects of the present inquiry was to examine the paramagnetic effect, if any, of intrinsically diamagnetic salts as compared with water, no allowance has been made for the negative susceptibility of any of the constituents, and the results are calculated for columns 4 and 5 of the table as if only the active constituent had any magnetic effect. By "active constituent" is meant the molecular proportion in a given salt of the sulphate of the magnetic metal concerned.

The product of the molecular weight and mass susceptibility χ_M has been given to four significant figures, but here again no reliance can be placed on the last numeral: in the case of ferric and chromic salts, half the molecular weight has been taken to bring them into line for comparison with the divalent salts.

The results are given in table 1 and special remarks will be found under the headings of the different metals. The general conclusions are then stated and the remarks concerning the anomalous results obtained from heated cobalt salts are given in a separate note.

No magneton numbers have been tabulated since Δ , in the Curie-Weiss equation, $\chi_M (T + \Delta) = C$, is commonly unknown and is probably positive in some and negative in others of the salts examined. An approximation to the magneton number may, however, be obtained either by the equation used by S. Meyer*, or by a modification which may be more simply written and easily remembered, viz: Weiss magneton number = $240 \cdot \sqrt{\chi_M}$, where the latter figure is expressed in c.g.s. units as in column 5 of table 1.

§ 5. REMARKS ON TABLE 1

Iron. Ferrous sulphate heptahydrate, and ferrous potassium and ferrous ammonium sulphates were dehydrated in a current of dried carbon dioxide to avoid oxidation; in this way white anhydrous salts were obtained. It is not possible to dehydrate ferric ammonium sulphate (iron alum) as it decomposes before dehydration.

It will be seen from column 4 of table 1 that ferrous sulphate has the highest value for its susceptibility in the form of ferrous ammonium sulphate, and next to it comes ferrous potassium sulphate both hydrated and anhydrous.

Anhydrous ferric sulphate has the low value of 57.4×10^{-6} rising to 75.45×10^{-6} in the form of iron alum. Magnetic dilution has evidently a great effect in both ferrous and ferric salts, and with the former both potassium and ammonium sulphate cause a greater increase in susceptibility than several molecules of water.

Manganese. In the sulphates of this metal the value of χ_M is increased only slightly by one molecule either of water or potassium sulphate, the maximum being reached with the greatest magnetic dilution in $\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$ or in $\text{MnSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$.

As manganese sulphate can be safely dehydrated by heating in air to about 300°C . its constancy renders it useful as a standard of reference, for when sealed in a glass tube it must remain unaltered indefinitely.

* *Phys. Z.* 26, 51-4 (1925).

Table I

Formula	Temperature (°C.)	χ for salt (10^{-6} units)	χ for active constituent (10^{-6} units)	χM (c.g.s. units)
<i>Iron salts</i>				
FeSO ₄	18.2	66.4	66.4	0.01008
FeSO ₄ ·H ₂ O	18	64.6	72.3	0.01097
FeSO ₄ ·7H ₂ O	17	42.4	77.6	0.01178
FeSO ₄ ·(NH ₄) ₂ SO ₄ ·6H ₂ O	17	32.3	83.4	0.01266
FeSO ₄ ·(NH ₄) ₂ SO ₄	18	42.8	80.0	0.01215
FeSO ₄ ·K ₂ SO ₄ ·6H ₂ O	17	28.2	80.6	0.01224
FeSO ₄ ·K ₂ SO ₄	18	37.3	80.05	0.01216
Fe ₂ (SO ₄) ₃	21	57.4	57.4	0.01145 for $\frac{1}{2}M$
Fe ₂ (SO ₄) ₃ ·6H ₂ O	19.4	58.0	67.3	0.01346 "
Fe ₂ (SO ₄) ₃ ·(NH ₄) ₂ SO ₄ ·24H ₂ O	21.5	31.3	75.45	0.01509 "
<i>Manganese salts</i>				
MnSO ₄	17.2	92.7	92.7	0.01399
MnSO ₄ ·H ₂ O	18	83.4	93.35	0.01409
MnSO ₄ ·4H ₂ O	19.4	66.8	98.7	0.01490
MnSO ₄ ·5H ₂ O	17.2	62.6	99.7	0.01506
MnSO ₄ ·K ₂ SO ₄ ·4H ₂ O	17	38.0	100.0	0.01510
MnSO ₄ ·K ₂ SO ₄	18	43.6	93.9	0.01418
<i>Cobalt salts</i>				
CoSO ₄ (heated in vac.)	18.5	61.6	61.6	0.009537
CoSO ₄ ·H ₂ O	17.5	56.7	63.3	0.009812
CoSO ₄ ·7H ₂ O	17.2	35.9	65.1	0.01009
CoSO ₄ ·(NH ₄) ₂ SO ₄ ·6H ₂ O	19	26.2	66.8	0.01035
CoSO ₄ ·(NH ₄) ₂ SO ₄	20	34.9	64.7	0.01002
CoSO ₄ ·K ₂ SO ₄ ·6H ₂ O	18	24.6	69.4	0.01076
CoSO ₄ ·K ₂ SO ₄	19	32.5	69.0	0.01070
ditto after 600° C.	20	34.3	72.87	0.01129
<i>Nickel salts</i>				
NiSO ₄	20	26.4	26.4	0.004085
NiSO ₄ ·H ₂ O	20.2	24.3	27.13	0.004198
NiSO ₄ ·6H ₂ O	20.2	16.7	28.4	0.004389
NiSO ₄ ·7H ₂ O	19	16.10	29.22	0.004520
NiSO ₄ ·K ₂ SO ₄ ·6H ₂ O	22	10.1	28.52	0.004413
NiSO ₄ ·K ₂ SO ₄	22	14.25	30.30	0.004688
NiSO ₄ ·(NH ₄) ₂ SO ₄ ·6H ₂ O	28.5	11.25	28.71	0.004442
NiSO ₄ ·(NH ₄) ₂ SO ₄	17	16.25	30.19	0.004661
<i>Chromium salts</i>				
Cr ₂ (SO ₄) ₃ ·5H ₂ O	18	24.5	30.2	0.005910 for $\frac{1}{2}M$
Cr ₂ (SO ₄) ₃ ·8H ₂ O	18	22.1	30.2	0.005927 "
Cr ₂ (SO ₄) ₃ ·K ₂ SO ₄ ·24H ₂ O	18.5	12.8	32.6	0.006390 "
Cr ₂ (SO ₄) ₃ ·K ₂ SO ₄ ·6H ₂ O	17	18.5	31.8	0.006241 "
Cr ₂ (SO ₄) ₃ ·K ₂ SO ₄	17.5	22.1	31.95	0.006261 "
Cr ₂ (SO ₄) ₃ ·(NH ₄) ₂ SO ₄ ·24H ₂ O	22	13.25	32.3	0.006335 "
Cr ₂ (SO ₄) ₃ ·(NH ₄) ₂ SO ₄	20	23.3	31.15	0.006110 "
<i>Copper salts</i>				
CuSO ₄	18.5	8.79	8.79	0.001397
CuSO ₄ ·H ₂ O	18.5	8.91	9.92	0.001577
CuSO ₄ ·5H ₂ O	18	6.13	9.62	0.001530
CuSO ₄ ·K ₂ SO ₄ ·6H ₂ O	18	3.26	9.05	0.001439
CuSO ₄ ·K ₂ SO ₄	18.5	4.69	9.83	0.001563
CuSO ₄ ·(NH ₄) ₂ SO ₄ ·6H ₂ O	18	3.61	9.06	0.001441
CuSO ₄ ·(NH ₄) ₂ SO ₄	17	4.56	8.37	0.001330

Cobalt. The value given for anhydrous cobalt sulphate was obtained from the salt after dehydration at 300°C . in a vacuum: further heating in a vacuum to 400° only increased its value of χ to 62.2×10^{-6} . The effect of heating in air to above 600° will be considered in the note on cobalt salts.

With cobalt sulphate as with iron the higher susceptibilities are exhibited by the cobalt potassium and cobalt ammonium sulphates, the effect of potassium sulphate on the anhydrous salt being distinctly greater than that due to a molecule of water of constitution, 69.0×10^{-6} to 63.3×10^{-6} .

Nickel. Nickel sulphate showed a rather smaller alteration in susceptibility but, like cobalt sulphate, showed the highest values for susceptibility when in combination with potassium or ammonium sulphate. It is unlike copper sulphate in that a single molecule of water is not sufficient to develop its full susceptibility and it requires at least $7\text{H}_2\text{O}$ to do so, whereas in the anhydrous state one molecule of potassium or ammonium sulphate will give a maximum susceptibility.

The most usual form of nickel-sulphate crystals appears to be $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$. The heptahydrate was specially crystallized at a low temperature. As the hexahydrate is dimorphous, crystallizing in both square prismatic and monoclinic forms, it cannot always be easily distinguished from the rhombic heptahydrate. Some confusion may result unless the water of hydration is carefully determined.

Chromium. It appears to be very difficult to obtain anhydrous chromic sulphate, methods given in the text-books having failed to give satisfactory results. It is useless to attempt to dehydrate the hydrated salt as it loses SO_3 , and a basic salt or ultimately chromic oxide results. But the double salts can be dehydrated by careful heating. Chrome alums show the highest value of susceptibility for chromium sulphate, which to a great extent is maintained in the anhydrous state. While potassium chrome alum forms a definite hydrate with $6\text{H}_2\text{O}$, ammonium chrome alum seems to be unstable at that degree of hydration.

On the whole, chromium salts show an even smaller variation than nickel sulphate under varying combinations.

Copper. Copper sulphate has been included in this examination, because although not a salt of a magnetic metal, it was one of the earliest in which the effect of hydration was studied. As the susceptibility is low the changes naturally are small, and in the case of normal copper-sulphate crystals the apparent susceptibility would be appreciably raised if the negative value of the four molecules of water of crystallization were taken into account. This modification has not been introduced into table 1 in order to maintain consistency with the results for other salts in which the diamagnetic effects of water or of potassium sulphate is of far less importance.

The highest susceptibility is given by the monohydrate, and this confirms the general results obtained by Feytis and by Gray and Birse to which reference has already been made. In the case of copper sulphate the influence of potassium and ammonium sulphates in increasing susceptibility is less than that of a single molecule of water.

Water. After measurement of the susceptibilities of copper salts with the weak suspension, a determination of the constant for water was attempted as a check on

the instrument and the standard of reference. After correction for the repulsion of the diamagnetic glass tube a value of -0.730×10^{-6} was found at a temperature of 18°C . This is not put forward in any way as a fresh determination for water but merely as a check on calibration: even in this respect it is not of much use as the coefficient for water has been so variously estimated, from the -0.689×10^{-6} found by Jäger and S. Meyer up to -0.79×10^{-6} obtained by Koenigsberger and by Curie and Cheneveau. P. Sève* in his report to the Congrès International d'Électricité in 1932 adopts the value found by Piccard and Devard of

$$-0.71993 \times 10^{-6},$$

or as a round figure -0.72×10^{-6} , as being accurate to 1 in 1000.

§ 6. CONCLUSIONS

It will be seen on reference to table 1 that when potassium sulphate is substituted for the water of constitution in the sulphates of iron, cobalt and nickel, there is a distinct increase in the susceptibility of the active constituent (column 4) and of the molecular susceptibility (column 5) which frequently persists and shows its effect in the fully hydrated double salts. This effect is very small but in the same direction in the case of manganese, but with copper sulphate a single molecule of water is more effective in increasing susceptibility than a molecule of either potassium or ammonium sulphate; in fact the latter, in the anhydrous salt, appears to act as a diamagnetic substance.

§ 7. A NOTE ON THE INCREASE IN SUSCEPTIBILITY PRODUCED BY HEATING COBALT SALTS

All values of susceptibility given in what follows are in 10^{-6} c.g.s. units.

In 1925 A. Serres† discovered that cobalt sulphate after having been dehydrated at a low red heat gave a susceptibility which indicated that it had 26 magnetons instead of the 25 previously assigned to it. In the following year A. Chatillon‡ published the results of experiments on cobalt chloride and referred also to cobalt sulphate. He found 26 magnetons in the case of anhydrous cobalt chloride and in a later paper§ reviews the whole subject and states that cobalt chloride in solution has been found with 22, 23, 24 and 25 magnetons and in the anhydrous state with 26.

Chemical knowledge of the ease with which most chlorides from that of magnesium upwards are hydrolyzed or oxidized would lead one to expect some such change on heating their hydrates especially in air. It was found that when cobalt chloride was dehydrated by gradual heating in air to 130° it gave a value of 90.75 for χ , but when it was heated in air to 200° – 230° values ranging from 101 to 105 were consistently obtained. These high values if referred to cobalt chloride alone would give it nearly 28 magnetons; but it was found in all cases in which this chloride showed exceptionally high susceptibility that when it was dissolved in water oxy-chloride was always deposited on standing, the amount of it being variable.

* *Science Abs.* 35, 5249 (1932).

† *Comptes Rendus*, 182, 765 (1926).

‡ *Comptes Rendus*, 181, 714–15 (1925).

§ *Annales de Phys.* 9, 187–260 (1928).

Dehydration in a vacuum produced by a mercury pump was then tried in order to exclude oxygen and to facilitate the removal of the water: this yielded an anhydrous chloride that although it had been heated to 230° gave a value of 91.2 for χ .

As it is well known that the addition of ammonium chloride to magnesium chloride prevents the hydrolysis of the latter salt on concentration and drying, the double salt $\text{CoCl}_2 \cdot 2\text{NH}_4\text{Cl}$ was prepared and after evaporation to dryness and heating in air to 130° the double salt gave a value 40.2 for χ corresponding to 73.5 for its contained cobalt chloride. Evidently the anhydrous cobalt chloride shows no specially high susceptibility in combination with ammonium chloride. The latter salt was then expelled by heating to 350° in a vacuum and after being cooled the residual cobalt chloride showed a susceptibility of 92.5. On solution in water it gave hardly a trace of oxychloride.

It must therefore be concluded that the value of χ for anhydrous cobalt chloride practically free from oxychloride is about 91 or 92, which justifies Chatillon's number of 26 magnetons. But in cases in which oxychloride is produced the susceptibility may evidently become considerably greater.

Nickel chloride furnishes confirmatory evidence, for when dehydrated in air at 200° it gave a value of 49.2 for χ , but when the dehydration was carried out in a current of dried carbon dioxide the value obtained was 37.5. The former figure would give a magneton number of over 19 while the latter would give only a little over the accepted value of 16: but even in this case the susceptibility of the anhydrous chloride is somewhat greater than for the same salt in solution.

It was found that although cobalt sulphate is fairly stable it slowly loses SO_3 when heated in air to temperatures above 600° and a basic sulphate is formed. This is rendered evident on solution of the salt after it has been strongly heated. When dehydrated in air at above 300° it yielded values of χ ranging from 63.2 to 66.2, but after dehydration in a good vacuum with a drying-tube attached the value of 61.6 given in table 2 was obtained. This figure was raised to 62.2 after further heating to over 400° *in vacuo*.

After this salt, previously dried at 300° , had been heated to a low red heat in air, values ranging from 75.6 to 83.5 were obtained for χ . As it appeared doubtful to what extent this increase in susceptibility might be due to the production of a basic sulphate, salts of a more fixed acid were examined.

Cobalt orthophosphate, $\text{Co}_3(\text{PO}_4)_2$, and pyrophosphate, $\text{Co}_2\text{P}_2\text{O}_7$, were prepared and dehydrated at 300° and their susceptibilities were determined. At this stage the former gave a value 76.6 for χ which for one third of the molecular weight gives $\chi_M = 0.009370$; and after it had been heated to a little above 600° the value of χ_M was found to be raised to 0.01008. But after being heated this salt became somewhat darker in colour, a fact which suggests the production of a small amount of cobalt oxide, as if at the high temperature some of the orthophosphate had been converted into pyrophosphate and cobalt oxide.

Cobalt pyrophosphate however was quite stable at temperatures considerably above 600° and became a lighter blue in colour: after dehydration at 300° its value

for χ was 67.3 but after it had been heated to 630° this value was raised to 81.4 which gives, for half the molecular weight, $\chi_M = 0.01188$ c.g.s. unit, a value equivalent to 26 Weiss magnetons or rather more.

Table 2

Formula	Maximum temperature attained (°C.)	Conditions	Temperature of measurement (°C.)	χ (10^{-6} units)	χ_M (c.g.s. units)
CoCl ₂	130	In air	17.5	90.75	0.01178
"	230	In air	18-22	101-105	0.01684 (mean)
"	230	<i>In vacuo</i>	18.5	91.2	0.01184
CoCl ₂ .2NH ₄ Cl	130	In air	17	40.2	0.009523
CoCl ₂ from above	350	<i>In vacuo</i>	18	92.5	0.01201
CoSO ₄	300	In air	17-20	63.2-66.2	0.010305 (mean)
"	300	<i>In vacuo</i>	18	61.6	0.009549
"	450	<i>In vacuo</i>	18	62.2	0.009642
"	630	In air	17.8	83.5	0.01294
Co ₃ (PO ₄) ₂	300	In air	18	76.6	0.009370
"	600	In air	18	82.4	0.01008
Co ₂ P ₂ O ₇	300	In air	18.5	67.3	0.009826
"	630	In air	18.5	81.4	0.01188
NiCl ₂	200	In air	20	49.2	0.006376
"	200	In dry CO ₂	18	37.5	0.004857

In some of these cobalt salts therefore there appears to be a true increase in susceptibility after they have been raised to a high temperature and in others there is also a spurious effect due to the production of oxychloride or basic salts, and it is very difficult to distinguish in some cases between these effects.

A NOTE ON DAVISSON'S ELECTRON-LENS FORMULAE

BY L. H. BEDFORD

Communicated by R. A. Watson Watt, May 1, 1934.

ABSTRACT. A simple proof of the Davisson electron-lens formulae is developed, and their proper interpretation is given for the important case of a lens system with differing entrance and emergence velocities.

§ 1. INTRODUCTION

C. J. DAVISSON⁽¹⁾ has published in two short abstracts in the *Physical Review* the results of an investigation of the electron-lens properties of an aperture in a conducting plane separating two regions of different electric field-strengths. The case contemplated is that of a conducting plane which in the absence of perforation has uniform electric fields E_1 and E_2 perpendicular to the plane on the two sides. An aperture is then made in the plane, without any other change in the system producing the fields. The aperture may take the form either of a long narrow slit (two-dimensional case) or of a circular hole (three-dimensional case). Davisson states that if the aperture is now irradiated with electrons it exhibits the properties of a thin lens of focal length given by

$$f = \frac{kV}{E_2 - E_1},$$

where

f is the focal length of the lens,

V is the velocity-voltage of the incident particles,

E_1 and E_2 (scalars) are the magnitudes of the field-strengths on the entry and exit sides before the perforation is made, these fields being reckoned positive when they accelerate the electrons, and

k is a constant having a value 2 for the two-dimensional case (cylindrical lens) and 4 for the three-dimensional case (spherical lens).

The object of this note is to show how the aperture comes to possess the properties of a thin lens, to derive a proof of Davisson's formulae, and to show how the formulae should be interpreted.

Suppose that a conducting plane P separates two regions of field-strengths E_1 and E_2 and suppose that E_1 and E_2 are both positive and $E_2 > E_1$. Before the aperture is made the equipotential surfaces are planes parallel to the plane P and the lines of force are straight lines normal to it. When an aperture is made in the

plane, having a size small compared with the dimensions of the system producing field, then in places remote from the aperture the field is not disturbed, but in the immediate neighbourhood of the aperture we have a transition region in which the field varies from E_1 to E_2 .

A complete and extremely elegant solution for the field distribution in the neighbourhood of a circular hole has been given by T. C. Fry⁽²⁾. However, the simplicity and generality of Davisson's results suggest that we do not need any such elaborate solution, but that the results must follow from general principles subject possibly to simplifying assumptions. Thus we may attempt to deduce Davisson's formulae from the general properties of an electric field subject to an abrupt transition. Now the vector field \mathbf{E} has to satisfy the condition $\text{div } \mathbf{E} = 0$ everywhere, and has to assume the values E_1 and E_2 on the two sides of the plane in regions

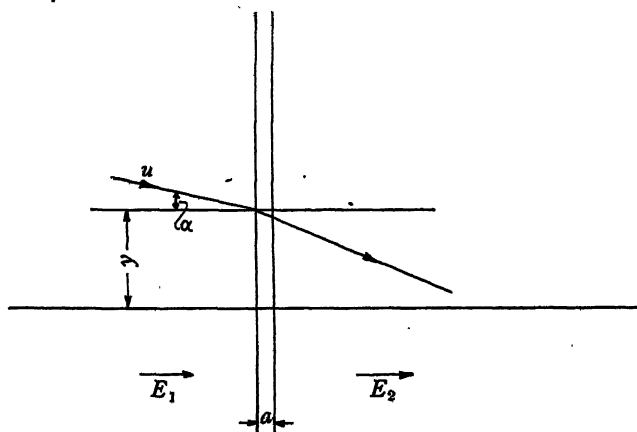


Figure 1.

remote from the aperture. Further, we shall have symmetry about the axis of the hole, or about the axial plane of the slit, in the three- and two-dimensional cases respectively. Let us represent this state of affairs by a field which has the value E_1 up to the plane $x = 0$, a transition from E_1 to E_2 over the slab of space between the planes $x = 0$ and $x = a$, and has the value E_2 for $x > a$, figure 1.

§ 2. THE TWO-DIMENSIONAL CASE

Here we have to consider a long narrow slit, which has the effect of a cylindrical lens.

The condition $\text{div } \mathbf{E} = 0$ may be written

$$\frac{\partial E_x}{\partial x} + \frac{\partial E_y}{\partial y} = 0;$$

also, since \mathbf{E} is derived from a potential,

$$\frac{\partial E_y}{\partial x} = \frac{\partial E_x}{\partial y}.$$

Then

$$\begin{aligned} dE_y &= \frac{\partial E_y}{\partial x} dx + \frac{\partial E_y}{\partial y} dy \\ &= \frac{\partial E_x}{\partial y} dx - \frac{\partial E_x}{\partial x} dy. \end{aligned}$$

If we assume $\partial E_x / \partial y = 0$, which is certainly true near the plane of symmetry,

$$dE_y = - \frac{\partial E_x}{\partial x} dy.$$

Assuming $\partial E_x / \partial x$ to be independent of y , which is likewise true near the plane of symmetry, we have

$$E_y = - \left(\frac{\partial E_x}{\partial x} \right) y,$$

y being measured from the plane of symmetry.

Now consider an electron entering the transition slab with velocity u at a distance y from the plane of symmetry, and moving at a small angle α to the axial direction. (This angle α and all other ray angles are assumed to be so small that it is not necessary to distinguish between the angle, its sine or its tangent. Likewise it is not necessary to distinguish numerically between the velocity u and its axial component.) During its travel through the slab the electron is subject to a force eE_y away from the axis, i.e. a force $e(\partial E_x / \partial x)y$ towards the axis. If we assume that the slab is so thin that the velocity u in the x direction is not appreciably altered within the slab, the time of travel through the slab will be a/u . The transverse momentum acquired is therefore

$$\int_0^a e \left(\frac{\partial E_x}{\partial x} \right) y \frac{dx}{u}$$

or

$$\frac{ey}{u} (E_2 - E_1).$$

The angular deviation of the ray is thus

$$\frac{ey}{mu^2} (E_2 - E_1),$$

which

$$\begin{aligned} &= \frac{ey}{2eV} (E_2 - E_1) \\ &= \frac{y}{2V} (E_2 - E_1). \end{aligned}$$

The electron ray thus receives an angular deviation proportional to its distance from the axial plane, which is exactly the property of a thin cylindrical lens in optics. In the optical case of a cylindrical lens of focal length f the deviation of the ray is y/f ; hence we see that in the electron lens

$$f = \frac{2V}{E_2 - E_1} \quad \dots\dots(1).$$

§ 3. THE THREE-DIMENSIONAL CASE

In this case we have a circular hole acting as a spherical lens. The condition $\text{div } \mathbf{E} = 0$ may now be expressed in cylindrical polar co-ordinates in the form

$$\frac{\partial E_x}{\partial x} + \frac{1}{r} \frac{\partial}{\partial r} (r E_r) = 0,$$

where r is measured from the axis of symmetry. On account of symmetry the third co-ordinate θ does not appear; $E_\theta = 0$. Also, since \mathbf{E} is derived from a potential,

$$\frac{\partial}{\partial x} (r E_r) = r \frac{\partial E_x}{\partial r}.$$

Then

$$\begin{aligned} d(r E_r) &= \frac{\partial}{\partial x} (r E_r) dx + \frac{\partial}{\partial r} (r E_r) dr \\ &= r \frac{\partial E_x}{\partial r} dx - r \frac{\partial E_x}{\partial x} dr. \end{aligned}$$

If we assume E_x to be independent of r (when x is constant),

$$d(r E_r) = -r \frac{\partial E_x}{\partial r}.$$

Assuming $\partial E_x / \partial x$ to be independent of r ,

$$\begin{aligned} r E_r &= -\frac{r^2}{2} \frac{\partial E_x}{\partial x}, \\ E_r &= -\frac{r}{2} \frac{\partial E_x}{\partial x}. \end{aligned}$$

Hence, proceeding as before, we find that the circular hole is analogous to a thin spherical lens and has a focal length

$$f = \frac{4V}{E_2 - E_1}.$$

§ 4. EFFECT OF CHANGE OF VELOCITY

In deriving the above results we have assumed that the transition zone is extremely short, so short in fact that the ray emerges with sensibly the same velocity-voltage as that with which it entered. Now in most practical applications this is not the case, and we therefore require to know how to interpret the Davisson formulae when the velocity of emergence differs from that of the entrance. This case will be illustrated in terms of a simple example, that of the double-disc accelerating lens. This example not only is itself very important in practice, but also is in a sense typical of all the practically important forms of electron lens. A double-disc lens, depicted in figure 2, consists of two circularly perforated discs separated by a distance d with the holes aligned on a common normal; electrons enter from one side with

a velocity-voltage V_1 and are accelerated between the discs to a velocity-voltage V_2 . Between the discs and "before the holes are drilled" there exists a field E_{12} equal to $(V_2 - V_1)/d$. On the entrance side we may assume a smaller field E_1 and on the exit side a field E_2 , usually zero. Davison's formula tells us that the first hole represents a lens of focal length f_1 , where

$$f_1 = \frac{4V_1}{E_{12} - E_1}.$$

The meaning of this focal length f_1 is that a parallel ray entering at a distance r from the axis is deviated inwards through an angle r/f_1 . This deviation is supposed to take place abruptly in the plane of the first disc. Thereafter the electrons pass through a sensibly uniform accelerating field whereby the axial velocity is increased in the ratio $\sqrt{(V_2/V_1)}$; consequently the inclination to the axis is reduced by this ratio and the angle at which it enters the second disc is $\sqrt{(V_1/V_2)}r/f_1$. At the second disc a further deviation occurs, and since $E_{12} > E_2$ this deviation is outwards; that is to say the second disc acts as a diverging lens. The angle through which the

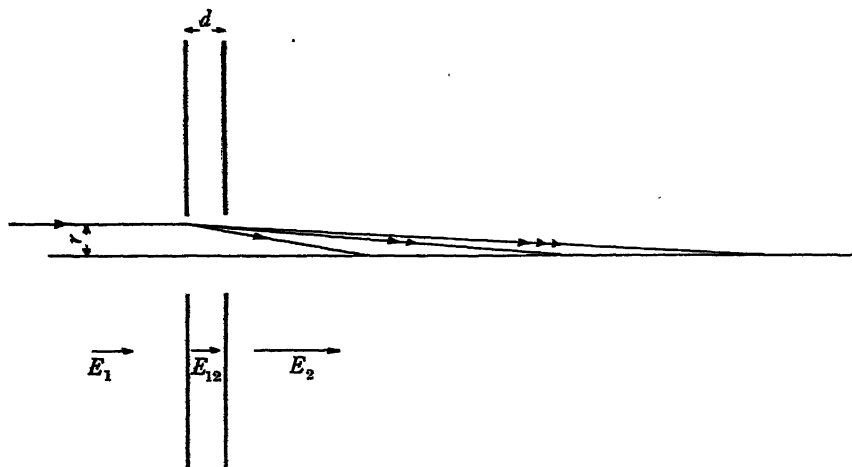


Figure 2.

ray is bent at the second disc is r/f_2 , where $f_2 = 4V_2/(E_2 - E_{12})$, a negative quantity. Hence, due regard being paid to signs, the final inclination of the ray on leaving the second disc is $\sqrt{(V_1/V_2)}r/f_1 + r/f_2$, and the total focal length of the combination is

$$\frac{1}{\frac{1}{f_1} \sqrt{\left(\frac{V_1}{V_2}\right)} + \frac{1}{f_2}} \quad \dots\dots(2).$$

In this form, however, the result is not of immediate importance because the ordinary geometrical construction for image and object does not apply; this is because, on account of the increase of axial velocity between the two discs, a centric ray is not undeviated.

In order to be able to apply the usual lens construction, which is particularly

significant for the reckoning of the magnification, we may envisage the effect of the increase of velocity as a compression of the scale of axial distance. Figures 3 and 4 make this clear.

In figure 3 is shown the actual state of affairs. The distance f is that given by the expression (2) above. In figure 4 the axial distances on the emergence side of the

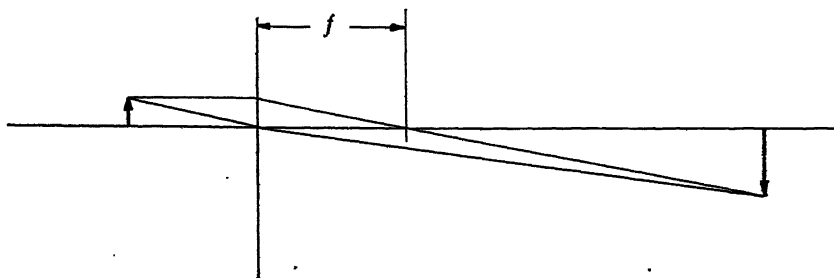


Figure 3.

lens have been divided by the factor $\sqrt{(V_2/V_1)}$; the centric ray is now undeviated and the ordinary construction applies. The (focal length) f' in this figure is

$$\frac{1}{\sqrt{(V_2/V_1)}} \cdot \frac{1}{f_1 \sqrt{(V_1/V_2)} + f_2}, \quad \text{or} \quad \frac{1}{\frac{1}{f_1} + \frac{1}{f_2} \sqrt{(V_2/V_1)}},$$

or

$$\frac{1}{\frac{1}{f_1} + \frac{1}{f_2'}},$$

where $f_2' = f_2 \sqrt{(V_1/V_2)}$.

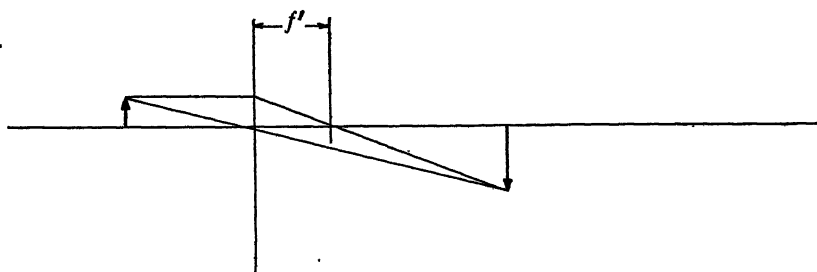


Figure 4.

This form of representation reminds us of the analogous optical case of a lens separating media of different refractive indices. The magnification reckoned in this way agrees with that found by von Ardenne⁽³⁾.

We may now work out the important case of the double-disc lens in which there is no field on either side of the lens but only the field $(V_2 - V_1)/d$ between the discs.

We then have

$$f_1 = \frac{4V_1 d}{V_2 - V_1},$$

$$f_2 = -\frac{4V_2 d}{V_2 - V_1},$$

$$f_2' = -\frac{4\sqrt{(V_1 V_2)} d}{V_2 - V_1},$$

$$\begin{aligned} \frac{1}{f'} &= \frac{V_2 - V_1}{4V_1 d} - \frac{V_2 - V_1}{4\sqrt{(V_1 V_2)} d} \\ &= \frac{V_2 - V_1}{4d} \cdot \frac{1}{V_1} \left\{ 1 - \sqrt{\left(\frac{V_1}{V_2}\right)} \right\}, \end{aligned}$$

$$f' = \frac{4V_1 d}{V_2 - V_1} \cdot \frac{1}{1 - \sqrt{(V_1/V_2)}}.$$

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IMAGE-DISTORTION DUE TO GLASS-THICKNESS IN LENS SYSTEMS. PART 2

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Communicated by William Taylor, F.R.S., February 28, 1934, and in revised form June 3, 1934.

ABSTRACT. The simplest method of applying the formulae given in part 1* is discussed. The formulae are applied to a Series V Cooke lens of 10-in. equivalent focal length. The effects of the three axial glass-thicknesses in producing fractional distortion in the final image or focal plane are ascertained by the application of two alternative but mutually confirming methods, the older and simpler of which is recommended for adoption.

My purpose in this second paper is to show that the correct procedure for arriving at the fractional distortion carried forward to the final image plane of a system of coaxial lenses and corresponding to any oblique principal ray traversing a parallel glass plate, is to work out first the fractional distortion produced by each parallel plate in its own second conjugate image plane. The algebraic sum of the several fractional distortions of all the parallel glass plates implied in the lens-thicknesses, together with the fractional distortions produced by all the lens elements, should vanish if the whole lens combination is to be rectilinear.

The theorem as stated in my *System of Applied Optics*, upon which the above method of summation rests, is that not only each lens element but each parallel plate also in its turn copies or carries forward to its second conjugate image plane any fractional distortional error existing in the second conjugate image planes of the preceding lens elements and parallel plates, at the same time adding its own fractional distortional error to those of all the preceding lens elements and parallel plates.

As, however, I began to feel some doubt regarding the validity, when the distortions arising in a lens system are summed up, of treating the distortions produced by parallel plates in exactly the same way as the distortions produced by the lens elements, I decided as a test to transfer the distortion effects of each parallel plate to the final focal plane by another method, as explained below, and find whether it justified the above-defined simpler method of summation as applied not only to the principal rays which are *angularly* deviated by the lens elements but also to the same principal rays when they are *side-stepped* by their passage through each of the parallel plates.

* *Proc. Phys. Soc.* 46, 283 (1934).

It is of course assumed at the outset that the image fields of all the simple lens elements and parallel glass plates involved in the lens combination to be dealt with are flat, according to the first-order or Gaussian assumption. If curvature of the image fields were to be taken into account, the resulting fractional distortion formulae would involve functions of $\tan^4 \chi$, $\tan^6 \chi$, etc., thus becoming formulae of higher orders.

Figure 1 is a section of the 10-in. E.F.L. Series V Cooke lens, which is utilized as an example for the application of the formulae numbers (1) to (3) of part 1 of this paper*. The specification of the glasses with radii of curves, axial lens-thicknesses and air spaces in inches is as follows.

L_1 and L_3 are of densest baryta crown glass with μD equal to 1.6114.

L_2 is of extra light flint glass with μD equal to 1.5482.

Radii	Axial thicknesses	Air spaces	Focal lengths of elements
$L_1 \begin{cases} r_1 = 1.457 \\ r_2 = 10.013 \end{cases}$	0.299	0.038	$f_1 = 2.38$ $f_2 = 16.56$
$L_2 \begin{cases} r_3 = -5.593 \\ r_4 = -1.327 \end{cases}$	0.046		$f_3 = -10.2$ $f_4 = -2.42$
$L_3 \begin{cases} r_5 = 101.2 \\ r_6 = 6.975 \end{cases}$	0.183	0.895	$f_5 = 165$ $f_6 = 11.41$

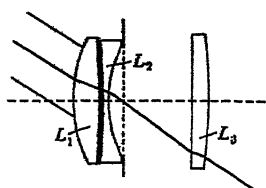


Figure 1.

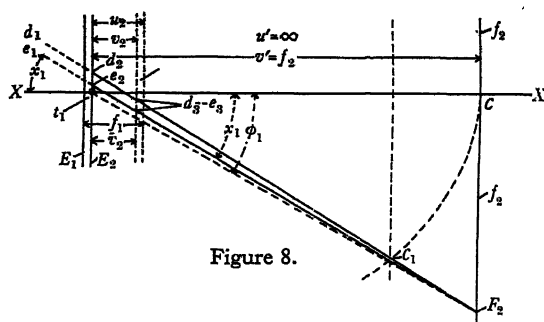


Figure 8.

In figure 8† E_1 and E_2 are the two elements enclosing the first parallel plate and $e_1 e_2$ is the principal ray (AA_1 of figure 3) which after refraction through the first element E_1 is refracted through the enclosed parallel plate and emerges from the latter lifted to the position $d_1 d_2$. It is then converged by the element E_2 to the oblique focus F_2 in its principal focal plane.

It should be noted here that I have assumed the rays of pencils entering the first element E_1 of the system on the left (shown dotted) to be parallel as if proceeding from a very distant object, and in figure 3 the dotted entering ray D_2 passes through the centre of the first lens element $E_1 \dots E_1$ without deviation, making an angle of $27^\circ 39'$ with the optic axis.

* *Loc. cit.*

† The numbering of the figures in part 1 has been retained in the present paper for convenience of references.

Then we have the condition that the ray $e_1 e_2$, figure 8, after emergence from the plate is lifted parallel to itself, thus becoming ray $d_1 d_2$, and the next problem is to find a formula which will define the effect of this lift in the *final focal plane* of the three-lens combination of figures 1 and 2.

Should it be required to allow for the curvature of the image field of E_2 , shown dotted, then the real oblique focus may be at or towards C_1 , but the formulae required to correct for such curvature of image deviations of the second, third, fourth, fifth and sixth elements would be expressed by smaller corrections of the next higher orders, in the shape of formula (2) or (3) of my last paper multiplied by a function of $f_2^{-1} (\tan^2 \phi_2)$, $f_3^{-1} (\tan^2 \phi_3)$, etc., resulting in corrections of higher orders $\tan^4 \chi$, $\tan^6 \chi$, etc., only required when exceptional accuracy is wanted, so that we may legitimately assume the images formed by pencils of parallel rays at the principal focal distances of the second, fourth and sixth elements also to be flat.

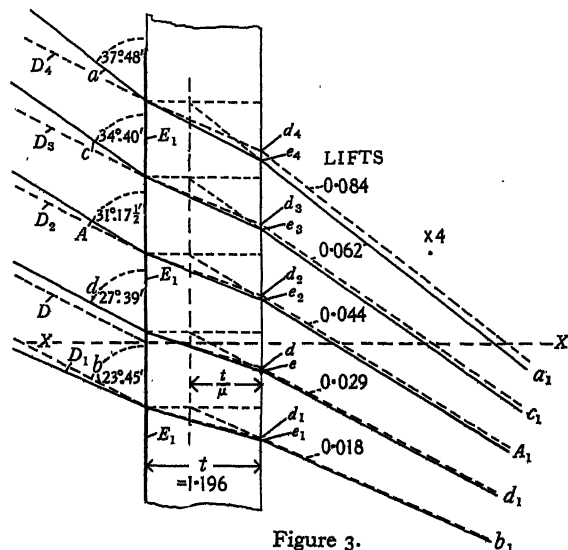


Figure 3.

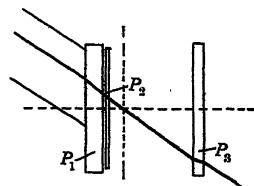


Figure 2.

But figures 8 and 10 suggest that the curvatures of image fields of some of the several elements may be considerable, besides increasing at an accelerating pace after angles of obliquity of about 30° have been reached. Thus the distortions of the next higher order due to such curvatures of image fields may become too serious to be neglected consistently with rectilinear projection and clear enough definition throughout the fields of view, in the case of photographic and projector lenses designed to give a half field of view of 35° or more. It should, moreover, be borne in mind that the curvature-of-field corrections of the six lens elements and three plates are balanced off against each other, in order to secure the final flat field.

Returning to the question of the effect in the final image plane of the distortion brought about by the first parallel plate involved in the first lens, illustrated in figure 8, we may note that the vertical lift $e_2 d_2$ of the principal ray $e_1 e_2$, figures 3 and 8, in this case is only 0.011 in.* and the hypothetical ray $e_1 e_2$ and the real lifted

* The lifts in figure 3 are four times exaggerated.

ray $d_1 d_2$ must be considered to focus or intercrossover at F_2 in the principal focal plane of E_2 , which is 16.53 in. behind e_2 . Clearly the projection angle between the two rays after refraction by E_2 is $(e_2 \dots d_2)/f_2$ or $0.011/16.53$ (in which f_2 is constantly expressed as its axial value $E_2 \dots c$ and not $E_2 \dots F_2$); this projection angle will become modified by each successive refraction through the remaining four elements. Therefore a formula is required for expressing the distortional effect of the original lift $e_2 \dots d_2$, when transferred to the final focal plane.

As u_2 and v_2 have so far designated the axial distances from E_2 of its two conjugate focal planes (-2.1975 and 1.9405 in the present case), then we may conveniently use the accented symbols u_2' and v_2' to designate the axial distances from E_2 of its conjugate focal planes when the rays e_1 and d_1 enter the element E_2 parallel, as in figure 8, so that $u_2' = \infty$ and $v_2' = f_2$.

It should be noted here that what I have named a "projection angle" is in itself a very inconstant quantity, as is explained by figure 12. It is clear that if $A_1 \dots A_2$ is the optic axis, C the centre of a lens element, and $a_2 \dots b_2$ a radial displacement in the

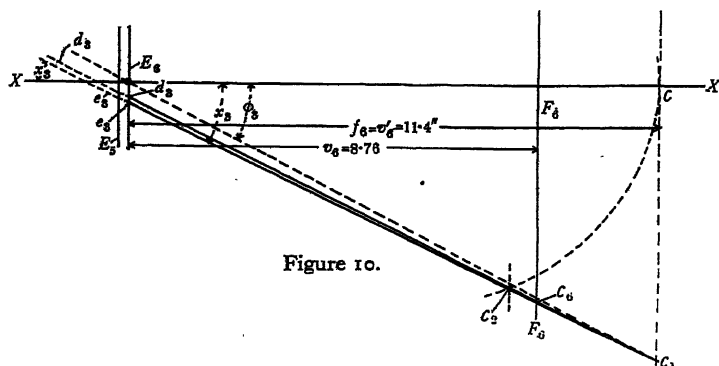


Figure 10.

first conjugate flat image $A_1 \dots a_2$ presented to lens element C , then the projection of $a_2 \dots b_2$ on to the second conjugate focal plane of C will become

$$a_2 \dots b_2 \times C \dots A_2/A_1 \dots C \text{ or } a_2 \dots b_2 \times v/u \text{ or } a_2' \dots b_2',$$

while $a \dots b \times v/u = a' \dots b'$ and so on. This first-order relationship holds good whatever the angles of obliquity χ_1 , χ_2 and χ_3 may be, although the projection angles ϕ_1 , ϕ_2 and ϕ_3 can be proved to diminish in proportion to $\cos^2 \chi$. Thus the factor $\cos^2 \chi$ can be ignored when radial displacements are transferred from the first conjugate focal plane of a lens element to their images in its second conjugate focal plane.

Then it is clear that the two rays converging to F_2 , figure 8, embrace a projection angle which is $e_1 \dots d_1/f_2$ or $0.011/16.56$ to start with. Similarly we may designate the vertical parallel lifts initially produced in the three parallel plates as l_1 , l_2 and l_3 respectively.

So the above angle starts as l_1/f_2 after refraction by E_2 ; this angle, enclosed between the two rays, becomes modified at each successive refraction by the following elements E_3 , E_4 , E_5 and E_6 , and a formula is required to express the linear amount of vertical displacement, towards or away from the optic axis, resulting when each of the two rays at last intersects the final focal plane to the right of E_6 .

In this case the vertical displacement in the final focal plane, caused by the first parallel plate, is

$$\frac{l_1}{f_2} \left(\frac{u_3' u_4' u_5' u_6'}{v_3' v_4' v_5' v_6'} \right) (v_6' + \text{b.f.l.}) \text{ or } E_1,$$

in which b.f.l. is the back focal length or the distance v_6 from E_6 to the final image plane.

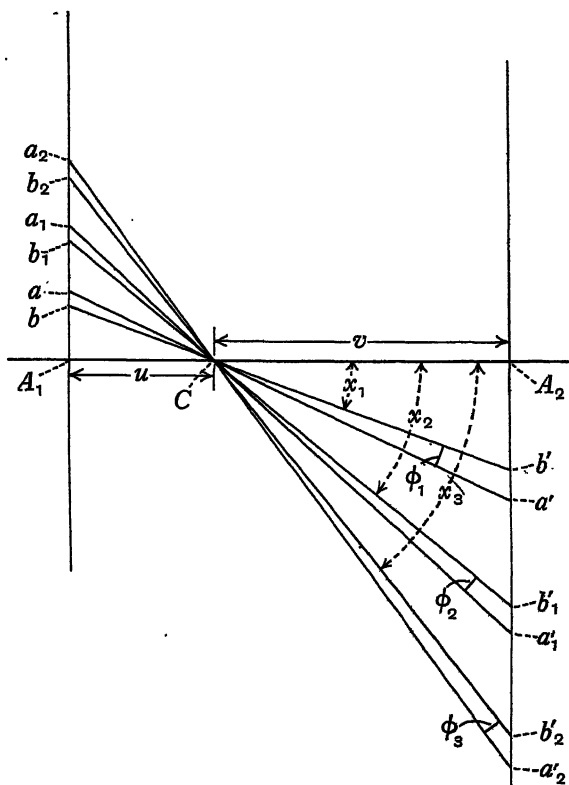


Figure 12.

After the u 's and v 's have been ascertained, this formula becomes

$$\frac{-0.01095}{16.654} \left(\frac{16.526 \times 26.68 \times 3.114 \times 3.288}{26.65 \times 2.219 \times 3.172 \times 4.62} \right) (4.62 + 8.758),$$

which
$$= (-0.01095) (0.3146) (13.378) = -0.046 \text{ in.}$$

of linear radial distortion in the principal focal plane of the 10-in. E.F.L. Cooke lens, or about $\frac{1}{20}$ in. of inward displacement from the correct position.

The fractional distortion produced by the first parallel plate is

$$\frac{-0.0461}{10'' \tan 27^\circ} = \frac{-0.0461}{5.096} = -0.00905 \quad \text{.....(D),}$$

which, in angular value, is about $24'$, or $\frac{1}{5}$ of the angular diameter of the full moon. This, in itself, would be a very serious amount of distortion in a photographic lens designed to give strictly rectilinear images.

It should be noted that figure 8 does not attempt to show the further course of the two rays e_1e_2 and d_1d_2 through the four following elements on their way to the final focal plane; otherwise the diagram would be undesirably complicated. But figures 9 and 10 show the simpler course of the rays resulting from the lifts l_2 and l_3 produced by the parallel plates enclosed in the second and third lenses of the combination shown in figure 1.

The case of the negative lens L_2 , figure 1, is illustrated in figure 9. Its centre thickness is only 0.046 in. and the appropriate formula is

$$\frac{l_2}{f_4} \left(\frac{u'_5 u'_6}{v'_5 v'_6} \right) (v'_6 + \text{b.f.l.}), \text{ or } E_2.$$

The angle of obliquity χ_2 here = $31^\circ 12'$ and the lift $l_2 = 0.00107$ in., so the formula in figures is

$$\frac{-0.00107}{2.4205} \left(\frac{3.316 \times 3.5}{3.383 \times 5.04} \right) (5.04 + 8.758).$$

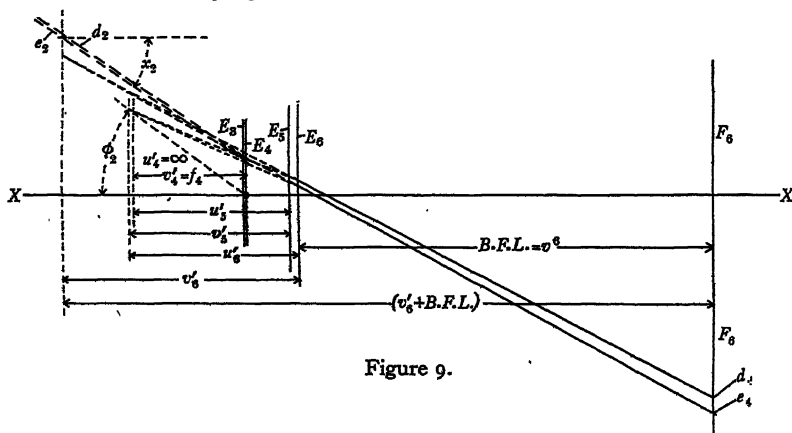


Figure 9.

This gives -0.00415 as the negative linear displacement in the final focal plane, or four times the original lift l_2 . The proportional distortion resulting from l_2 is

$$\frac{-0.00415}{10'' \tan 27^\circ} \text{ or } \frac{-0.00415}{5.096} \text{ or } -0.0008,$$

corresponding to $-2'$ only.

The parallel plate of the third lens yields a linear distortion E_3 expressed by

$$l_3 (f_6 - v_6) / f_6 \text{ which } = -0.0056 (11.41 - 8.76) / 11.41 = -0.0013 \text{ in.}$$

But $-0.0013 / 10'' \tan 27^\circ = -0.00026$, corresponding to about $\frac{1}{2}'$, so the effect here is negligible.

This last case is illustrated in figure 10, in which E_5 and E_6 are the two element planes of the third lens, enclosing between them the third parallel glass plate, while $c \dots c_1$ is the principal focal plane of E_6 , and $c \dots c_2$ is the curvature of its field (probably exaggerated). Then e_3 and d_3 are the original and lifted rays, respectively, entering E_6 parallel and then refracted to c_1 in the principal focal plane of E_6 . But if the curved field (dotted) of E_6 is taken into account it is clear that the rays d_3 and e_3

will intercross at c_2 and then diverge again onto the final focal plane, f.f.p., at c_3 so that the linear distortion will be reversed in sign and become positive, although its amount will be still more negligible.

Thus the total distortion for all three parallel plates amounts to $-27\frac{1}{2}'$ at $27^\circ 39'$ from the centre of the field, an amount of distortion which, were it not approximately neutralized by a positive balance of the other distortions brought about by the six lens elements, would be scarcely tolerable in any photographic lens claiming to be rectilinear.

Now we are in a position to see whether this special method of translating the parallel lift of the principal ray $e_1 \dots e_2$, caused by the first parallel plate, to its fractional distortional effect in the final image plane confirms the simpler and more convenient copying-through theorem, defined at the commencement of this paper.

We found that the exact or trigonometrical value of the lift occurring in the first parallel plate (enlarged four times in figure 3 for the sake of clearness) was 0.011 in., causing a fractional distortion in the final image of -0.00905 as worked out by the more elaborate testing method herein used.

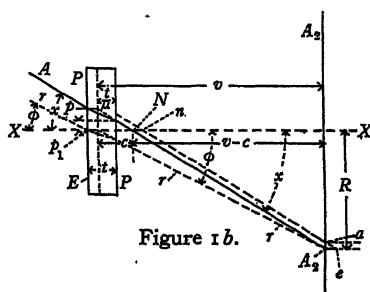


Figure 1b.

Now figure 1b illustrates the simpler copying-through method, and its formula in this case expresses the fractional distortion in the field of the first element E caused by the lift of the principal ray consequent on traversing the first parallel plate. The formula takes the shape

$$\frac{\text{Trigonometrical value of lift}}{(v - c) \tan \chi}$$

(see figure 1b), where v , the principal focal length of the first element, $= 2.38$ in. and c , figure 1b, is the axial distance (about 0.38 in. behind $E \dots P$) at which the principal ray $A \dots A_1$ in figure 3, or $A \dots A_2$ in figure 1b, crosses the optic axis after being refracted by the first lens element $E \dots P$. The original beam of parallel rays D, D_1, D_2, D_3 and D_4 , shown dotted in figure 3, enters the first lens element at an angle of $27^\circ 39'$ to the perpendicular, or to the optic axis $X \dots X$. The ray D_2 after refraction by the first lens element E_1 then takes the direction indicated by the full line above D_2 to the left of the first element $E_1 \dots E_1$ and then enters and leaves the parallel plate, making an angle of $31^\circ 17\frac{1}{2}'$ with the optic axis $X \dots X$. The refraction by the first element has thus changed the original $27^\circ 39'$ of obliquity to $31^\circ 17\frac{1}{2}'$. We have seen that the essential algebraic formula for expressing the fractional or

proportional distortion in the image plane projected by the element E_1 through the parallel plate is

$$\frac{\text{Vertical lift of ray } A \dots A_2}{(v - c) \tan \chi}$$

as illustrated in figure 1*b*, where the vertical lift

$$= t \left\{ \frac{\mu^2 - 1}{2\mu^3} \tan^3 \chi - \frac{3(\mu^2 - 1)^2}{8\mu^5} \tan^5 \chi + \text{etc.} \right\}$$

and the fractional distortion is therefore

$$\frac{t}{v - c} \left\{ \frac{\mu^2 - 1}{2\mu^3} \tan^3 \chi - \frac{3(\mu^2 - 1)^2}{8\mu^5} \tan^5 \chi + \text{etc.} \right\}.$$

For the sake of clearness we have indicated in figure 3 four times the correct lift imparted to the principal oblique ray $A \dots A_1$. For the 0.044 in. shown is four times the trigonometrically calculated value, and should be 0.011 in. so that 0.011 in. supersedes in this case the algebraic series of terms in the upper line of the last formula. This expression becomes $-0.011/(2.38 - 0.28) \tan 31^\circ 17\frac{1}{2}'$, which is the same result as (D) previously obtained by the more complex method. The fractional distortion is $-0.011/2$ (0.6078) or -0.00905 , so that the fractional distortion produced by the first parallel plate in the image projected through it by the first element has been exactly copied through to the final focal plane of the lens combination.

Therefore the more simple and convenient copying-through theorem holds good for the fractional distortions of the parallel plates as well as for the lens elements.

AWARD OF THE DUDELL MEDAL, 1934, TO HAROLD DENNIS TAYLOR, F.R.S.

Address delivered by Prof. A. O. Rankine, F.R.S., President, March 16, 1934.

THE Council of this Society announced in December 1933 the Award of the Duddell Medal to Harold Dennis Taylor. It is now my very pleasant duty on behalf of the Society to present this medal to him.

This is by the regulations awarded to persons who have contributed to the advancement of knowledge by the invention or design of scientific instruments, or by the discovery of materials used in their construction. So soon after the amalgamation of the Optical Society with the Physical Society of London to form the Physical Society it is a happy coincidence that, on this occasion, the recipient should be a very distinguished investigator in the field of optics.

Mr Taylor has lived and worked in a period of the first importance in the development of optical instruments. A few investigators, notably W. Vernon Harcourt, had realized during the last century the nature of the principal problems to be solved, and might have been successful had it been possible then to manufacture the necessary types of glass. When the new Jena glasses became available for general use forty years ago, Dennis Taylor was ready to seize upon and make splendid use of the opportunities thus afforded. At that time he was the Optical Manager of Thomas Cooke and Sons of York, a firm justly celebrated for its astronomical and surveying instruments. Large astronomical refractors suffered at that period from a serious defect, known as the "secondary spectrum", which remained when the normal conditions for the removal of chromatic aberration had been satisfied. The Jena glasses provided the means for the practical elimination of this defect, and the first opportunities of using them for this purpose naturally fell to Abbe and his co-workers, who produced some apochromatic telescopic doublets. Taylor resorted to a different solution. He employed three glasses, and with rare skill and insight devised an objective in which much more than the pure optical problem was solved. Telescopes constructed to this design of Taylor's, the first triple apochromats, have met with great success. Their colour correction is so good, and is so successfully combined with the other five corrections needed, that the same instrument may be used both for visual and for photographic work. They are correctly described by their name, "photo-visual objectives." Moreover, Taylor has been more fortunate in his design than Abbe. The former used glasses of moderate, the latter of extreme properties. These extreme glasses proved to be unstable, so that instruments incorporating them deteriorated rapidly, while several of Taylor's 12-in. refractors remain still in regular use.

I turn to Dennis Taylor's next great invention, the one with which his name will always be most closely associated. In 1893 he took out two patents for photographic

lenses which were later put on the market and became justly celebrated all over the world as "Cooke lenses." Their production was placed in the hands of Messrs Taylor, Taylor and Hobson of Leicester, of which firm it should be said that they manufactured the lenses so carefully and accurately that the user really enjoyed in his camera the qualities attainable from their design.

It is impossible here to discuss in detail the principles on which the lenses are constructed or even to convey an adequate idea of the beauty of the design ultimately reached. The specifications of the lenses are notable documents of high scientific value, and their importance may be judged from the fact that four official editions of them have appeared, the last nearly forty years after the patent was granted. These lenses showed how fully Dennis Taylor was master of the theory of the aberrations of lenses. In the specifications of the Cooke lenses nothing is more striking than the treatment of the theory which leads to the method of eliminating coma simultaneously with curvature and astigmatism.

If any further tribute were needed for the great qualities of these lenses, it would be afforded by the way in which they have been imitated in other lands since the expiry of the master patents, and not least by the adoption of Taylor's design for the very large photographic lenses made in Germany during the War for aerial photography.

In later years Mr Taylor has not lost the skill he displayed in his earlier inventions. Special mention should be made of the telescope in which he showed how it is possible to combine a large aperture and a large field of vision with freedom from aberrations comparable with that attained in the Cooke lenses. This is an achievement of the first order.

Optical instruments of the highest quality are no less essential for the progress of most experimental sciences than they are for many of the arts. Telescopes large and small and photographic lenses are among the indispensable tools of the physicist. The optical work of Mr Taylor places him indisputably in the front rank of those whose labours have served the advancement of knowledge. His work has been of such outstanding quality as richly to merit the recognition which the award of the Duddell Medal signifies.

Mr Dennis Taylor, in the name of the Physical Society, I ask your acceptance of the eleventh Duddell Medal and Certificate, at the same time expressing the hope that you will live long to make still more smooth the paths of scientific investigators.

GUTHRIE CENTENARY

Address delivered by Prof. A. O. Rankine, F.R.S., President, October 20, 1933.

FREDERICK GUTHRIE was born on October 13, 1833. To-day is the first meeting of the Physical Society following the centenary of his birth, and I have been asked by the Council to make a few remarks on the man and his work, as it is not proposed to celebrate the occasion in any more elaborate manner. We already remember Guthrie at least once a year in the institution of the Guthrie Lecture. The first of these annual discourses was given in 1915 by Prof. R. W. Wood, and I understand that reminiscences of Guthrie were given then, although owing to an unfortunate oversight neither these nor the lecture were published. But we are not without records in our *Proceedings*, and recently I have perused them with great interest. We have first the memoir by Prof. Carey Foster, shortly after Guthrie's untimely death in 1886, appearing on page 9 of the *Proceedings* of the session 1886-7. Then most of us had the pleasure also, during our Jubilee Celebrations in 1924, of hearing tributes to Guthrie from the lips of such men as Sir William Barrett, Sir Ambrose Fleming, Prof. Boys, Prof. Armstrong and Sir Oliver Lodge, all of whom had known our founder personally. I take this opportunity of referring you again to the record published in the special Jubilee number of the *Proceedings*, because it is impossible for me, belonging, as I do, to a younger generation, to add anything really pertinent.

What struck me most were some words of Carey Foster which I shall quote. He said "It is seldom that a scientific Society owes its existence so distinctly to the action of one man as the Physical Society of London owes its origin to the action of Frederick Guthrie." That is the principal reason why our Society honours him. He was a good physicist, and the better, according to Prof. Armstrong, for having been first a chemist and remaining one at heart all his life. As a teacher he was in the first rank, indeed a pioneer in the development of the practical side, as might have been expected from his devotion to experiment. But it is not primarily on these grounds, or even for his notable contributions to knowledge, that we mark the centenary of his birth. It is because of the unselfish zeal with which sixty years ago, in spite of some opposition and discouragement, he gathered together the nucleus of our Society, and promoted its interests ardently until he died. No one can doubt that the splendid growth in numbers and usefulness has fully justified Guthrie's aims, and we count ourselves happy to be able to continue to build upon the foundation which he laid.

There are no rival claimants, and I ask you to stand with me for a few moments as a token of our heartfelt esteem and remembrance of Guthrie, the founder of our Society.

OBITUARY NOTICES

PROF. A. P. CHATTOCK, F.R.S.

THROUGH the death of Emeritus Professor Arthur Prince Chattock, M.I.E.E., D.Sc., F.R.S., on 1st July last in his 74th year, the Society has lost an old Life Member who first joined it in 1884.

Temperamentally very self-effacing and modest, he was personally unacquainted with most of the Fellows, but those who knew him intimately or followed the record of his work in detail recognized him to be an experimenter of the first rank and a pioneer in every field that he entered. In the early eighties of last century he was investigating the possibilities of human flight and measuring the resistance offered to rotating vanes. His experiments and calculations led him to the conclusion that flight was impracticable unless some substitute for a steam engine as motive power could be found. The year 1887 found him at Liverpool insisting, before the discoveries of Hertz, as Sir Oliver Lodge relates, that the oscillatory discharges of a Leyden jar then under investigation by the latter ought to be accompanied by electric waves. A perusal of an early note-book of his, dated 1890, has recently shown that behind his well-known experiments on point discharge was an attempt to determine the ratio of the mass of an atom to its charge. The attempt was unsuccessful at the time, though he collects in his book the evidence that it gave him of the constancy of the atomic charge. In a paper on the energy of the Amperian molecule, which he published jointly with F. B. Fawcett in 1894, he was led to conclude that if magnetism had its origin in rotating electric charges this rotation was not necessarily associated with the rotation of the molecule as a whole. The discovery of the electron a year or so later filled the gap in the picture. His last important work in pure physics was also in the field of magnetism, when he made his classical determination with L. F. Bates of the gyro-magnetic ratio for iron in 1923. This was a marked experimental achievement, the final accuracy within 1 per cent being many times greater than that of any previous experimenters.

To watch him work was to realize that he had the hands of a true experimenter and a real mechanical sense. This was shown in the design of several instruments. He was one of the earliest to apply extensively the principle of measuring small forces by balancing them against a tilt. He used a high-potential electrostatic voltmeter of this design in 1891* and again applied it in the same paper to measure the field at the surface of a discharging point. It was also an important principle in several gauges that he used in his work on the pressure of the electric wind, which culminated finally in the Chattock-Fry gauge originally designed for Stanton's work on the pressure of wind on buildings†. It was this instrument, by far the most sensitive that was available at the time, which first enabled an insight to be obtained

* *Phil. Mag.* 32 (1891).

† *Proc. Inst. C.E.* 186.

into the way in which the normal pressure varies over the surfaces of aeroplane wings and stream-line bodies. It also made possible the first accurate calibration in this country of the standard Pitot static tube, a determination to which all subsequent air-speed measurements have been referred. Another ingenious instrument, which he sometimes jocularly referred to as the best thing he had ever done, was a magnetic potentiometer devised in 1887*. This device has recently been resuscitated for use by Bates† and also by C. D. Ellis.

During a period of retirement into country life he carried out a comparison of the humidity, air flow and other physical conditions under a sitting hen and in an incubator. His paper on this subject‡ gives several illustrations of his experimental skill, for he had to devise apparatus which would not in any way disturb the hen, any bodily movement of which would have vitiated the results.

He was originally trained at University College, London in electrical engineering under Alexander Kennedy, and in physics under Carey Foster, 1879–84. Throughout the greater part of his academic career he was associated with the Physics Laboratory at Bristol, first as a demonstrator 1885–87, then as Lecturer and Professor 1889–1910, and finally as Emeritus Professor and Research Fellow 1919–24. He received the honorary degree of D.Sc. of that University in 1911, and was elected a Fellow of the Royal Society in 1921. Shortly before his final illness the Council of the University decided to create a permanent Chattock Research Studentship in Physics in recognition of his invaluable services.

Until his retirement from the Chair in 1910, the students at Bristol were fortunate in possessing a teacher of outstanding ability, whether in the lecture room or the laboratory, and one who made many great sacrifices in their interests. To those who were at one time young research students under him his inspiration, personal example, and generous friendship will remain a vivid memory.

A. M. TYNDALL

* *Phil. Mag.* 24.

† *Proc. Phys. Soc.* 45, 425 (1933).

‡ *Phil. Trans. B*, 213 (1925).

SIR W. B. HARDY

SIR W. B. HARDY died on January 25, 1934. It is unnecessary here to comment on the many characteristics of his engaging personality, his breeziness, his energy, or his great versatility. This has been done adequately elsewhere, but it is proposed in this short note to indicate some of his contributions to physical science. Mention must be made of Hardy's pioneer work on colloids. He was the first to point out the importance of the electric charge on the particles as a factor in preventing their adherence and hence their coagulation, the latter taking place when the charge is nearly removed. The word "pioneer" may with justice be applied to his work on the spreading of films on water. In two papers presented to the Royal Society in 1912 and 1913 on the spreading of various substances on the surface of water Hardy suggested that the arrangement of the molecules of a pure liquid might be different at the surface from the random distribution in the interior, and suggested that if the force-field about a molecule is not symmetrical then the inwardly-directed attraction along the normal to the surface would cause orientation of the molecules there. He visualized the surface film as having a characteristic molecular architecture, the condition of minimum potential involving two terms, one relating to the variation in density and the other to the orientation of the fields of force. Another paper of considerable originality was on "the application of the principle of dynamical similitude to molecular physics." The principle was applied to the internal latent heat of evaporation of a liquid, and subject to certain assumptions it was shown that the potential energy of the repulsive forces acting between the molecules contributes to the process of evaporation.

In the Guthrie Lecture delivered before the Physical Society in 1916 Hardy discussed the physical aspects of certain phenomena of living matter.

In conclusion, mention must be made of Hardy's work on static friction and lubrication. This formed the subject of his Bakerian Lecture to the Royal Society in 1925. He resurrected a law, first put forward by Amontons as long ago as 1699, to the effect that in external friction the resistance to relative motion is independent of the area of the applied surfaces and varies directly with the force or load which presses them together. Experiments with a very large number of substances showed that the static friction is independent of the manner in which the lubricant is applied and of the quantity present, provided there is sufficient to form a primary film over each face. With a spherical slider on a plane surface Amontons's law was found to hold for a fifty-fold increase of load. The value of the coefficient of friction was found to be a function of two variables, the nature of the solid face and the chemical nature of the lubricant. Within the same chemical series it was found to be a linear function of the molecular weight and to decrease as the molecular weight increased.

IDA BIRCUMSHAW

REVIEWS OF BOOKS

Faraday (1791-1867), by THOMAS MARTIN (*Great Lives*, No. 40). Pp. 144. (London: Duckworth and Co., Ltd.) 2s. net.

Mr Martin is well known as Secretary of the Royal Institution and as Editor of the *Faraday Note-Books*; writing with a refresher from the Faraday papers in the custody of the Institution, he now presents in this volume a fascinating, all too brief account of the philosopher's life. The book is one to have and to hold; if books of worth were in demand at the bookstalls, it would be upon them all and freely read by the intelligent. A more elevating life is not to be found—upon no other model can we better shape our future action.

Huxley and others have talked of catching "potential Faradays" through technical education—can it be done? What would they give us? If the public have no measurement sense for money values—President Roosevelt shows this—how shall it evaluate mental and moral worth? How are we to measure the value of the man who first made electricity work—whose barely seen electromagnetic induction spark of 1831 holds the world in thrall to-day? Now endlessly enlarged, if it does not serve to move mountains, it thriftily uses their slopes by making the running waters of the world everywhere the servant of man, so putting the countries without storage of sunshine on a par with those that depend upon combustible fuel. Oil may come and oil may go, but rivers will run for ever: so long as they do, we may count upon living in amber security.

Faraday's name, however, is little known in the schools and unmentioned in pulpits. Even electricians have little thought of his work: they are content to enlarge his spark. By common consent, says Mr Martin, he is one of the great figures in English science. Who cares for such figures? The schools worship only those of antiquity. Faraday is far more than a great figure: taking into account both the ethical example of his life and his specific work as a discoverer, weighing works against words, we are justified in rating him *the greatest figure* in modern times and no such figure could exist previously. We have yet to secure for him his right place in society to give him a popular value.

Whatever impetus he may have given to the art of experimental inquiry, the worth of the spiritual example he set by his manner of working, studied in detail, is of far greater account—if only we will take it to heart—if there be enough of greatness in us to value the great. Probably the most weighty lecture ever delivered at the Royal Institution is that which Faraday gave, on May 6, 1854, before his Royal Highness, the Prince Consort of Queen Victoria—a most worthy listener—*On Mental Education*. It is printed in the volume of his collected papers on Chemistry and Physics. A better title would have been *On the Formation of Proportionate Judgment*. The doctrine set out in the lecture is embodied in his own early definition of the "natural philosopher," the term by which he preferred to be known. This Mr Martin quotes, as follows:

The philosopher should be a man willing to listen to every suggestion but determined to judge for himself. He should not be biased by appearances; have no favourite hypothesis; be of no school and in doctrine have no master. He should not be a respecter of persons but of things. Truth should be his primary object. If to these qualities be added industry, he may indeed hope to walk within the vale of the temple of nature.

Some day we shall evolve from this lecture a few special commandments, a catechism and a set of collects, to be learnt and recited daily in schools: then inklings of scientific method may begin to dawn in the mind of the community. We have passed from the Iron

Age into the Amber Age through Faraday's act. Seeing that he has done so much to lead the world into communication and to carry us about by rail- and tram-way, maybe the public will eventually be led to take as much interest in his life as it now does in a Test Match or in the life of a deceased Prime Minister, even in the tales told by a Prime Minister's wife. To this end, someone has to write a real book around the man and his work, up to say the end of the fifth series of experimental researches (June 1834). Such a work might be made of the greatest educational value, in laying electro-chemical foundations.

Can Faraday be "explained"? Mr Martin's reading is scarcely satisfactory; he begins his book by saying:

The mystery of heredity, the difficulty of finding in parents any evidence of the qualities of their children, was never better exemplified than in the birth and parentage of Faraday. His life's work was one of the most astonishing outpourings of natural genius the world has ever seen... his kingdom of natural philosophy was his by right of conquest and not by inheritance. His powers of intellect were his own. His family history shows no trace, among immediate forbears, of any predisposition to science or of intellectual attainment in any direction above the ordinary. Nor did he owe anything to training of the orthodox kind. His parents were poor and unable to give him any advantages in schooling. He was almost entirely self-taught. His education and scientific training followed no regular plan but were the outcome of his own interest in scientific things and desire to escape from trade and follow a scientific calling. It cannot even be said that he owed much to the example of others.

As to heredity—his father was a blacksmith and his uncles were all practical men: one a farmer, another a grocer, a third a shoemaker; his mother was a farmer's daughter; his elder brother a blacksmith who became a gas-fitter when gas was introduced as an illuminant: to-day he would have taken up electrician's work and wireless. His relations were therefore practical people: they had fingers and all took up independent careers, above the ordinary. Surely, we may regard both smithing and farming as sciences of a high order—the best of stock upon which to graft the desire to know: apparently, Faraday's early characteristic. As an apprentice he showed a desire to use both his fingers and his eyes, spending much time in drawing and showing no slight appreciation of graphic art. The sketches in his note-books, as Mr Martin points out, are evidence of his skill.

Leaving school at thirteen, he began to carry round newspapers. A year later, he was apprenticed as a book-binder. He thus learned to work and bound books not only in boards but into himself—he became an avid reader and had good books to read. For some reason undisclosed he had an inquiring mind; this was his making: it is probably the one essential to success in all walks of life. The modern boy of his age has little practice with his fingers and leads a lotus life at school, constantly tutored and confined in his outlook by the need of passing this and that examination. The inquisition of school and university is now such as to deprive boys and girls of all sense of freedom of thought. The idea that they must reach a high standard of verbal proficiency in this, that and the other subject—the neglect to develop faculty—the low standard of practical teaching and entire disregard of the soil—these together rip soul and individuality out of the great majority. We ruin the potential Faradays.

Faraday may be said to have been peculiarly happy in his early schooling, and his training after he entered Davy's service was ideal—a prolonged course in the art of pure discovery. Not only did Davy take him abroad and introduce him to the great workers of the day, but he set his assistant a wonderful example—by studying on his travels, in his bedroom, the new substance put into his hands in Paris, and at the end of a week recognizing in it a new element, which he named "iodine." Then, by using the great lens at Florence, he burned the diamond, for the first time, in oxygen, proving it to be carbon. Later came the discipline of the experiments which led to the safety lamp. Faraday must

have participated in Davy's joy of discovery: we can be sure that the master was never reticent in the display of his satisfaction.

Nevertheless, he developed but slowly as an independent worker. His first serious experimental work—that on alloys of iron, only recently disclosed by Sir Robert Hadfield—was not begun until 1818. His first prolonged philosophical inquiry was that involving the comparison of electricities and the study of electrolytic phenomena, begun in 1831, and lasting until June 1834. In other words, he was full forty years old by the time he had felt his way into his subject and made himself a finished, logical worker. His notebooks show that he had an infinite capacity for taking pains: herein lay his genius. He had the inestimable advantage of being a pioneer, for the most part in an open field, unprejudiced by any great burden of existing knowledge. The freedom he enjoyed, coupled with his great obstinacy of purpose, accounts for a large measure of his success.

Out of scientific bounds, he was intensely prejudiced by home training. In his day, youth was brought up severely on Sundays. The Faradays were a religious family, members of a peculiar sect, the Sandemanians (Glasites), a body which accepted the Bible literally. Faraday held this faith and apparently without question: this is the more remarkable, as he was without mathematical bias and unable to let anything be granted without proof—witness the experiments on “table turning.”

Owing to the continued retention in our schools and universities of ecclesiastical methods, doctrine and dogma are now almost universally taught and freedom of thought comes only to the few. The fact is, much as we know, we are unable as yet to overcome our human nature—man's infinite gullibility and clerical fixity of mind.

The present state of society—the world dominance of mechanism rather than of mind—would seem to be due to our failure to develop the sense of proportionate judgment, upon which Faraday laid such stress, as well as to the never ceasing indoctrination of dogma.

H. E. ARMSTRONG

Planetary Theory, by ERNEST W. BROWN and CLARENCE A. SHOOK. Pp. xii + 302. (Cambridge University Press). Price 15s. net.

Prof. Brown is pre-eminent among living authorities on celestial mechanics, and this volume, which he has written in collaboration with a distinguished fellow-worker in the same field, is not only a very important addition to the rather limited range of modern textbooks available for the student, but also a valuable contribution to the original literature of the subject. The authors have not set out to write a general treatise on dynamical astronomy or an exposition of the chief classical developments of planetary theory, but have in the main restricted themselves to giving a full and detailed account of two principal modes of procedure. Of these, one employs the method of changing the variables to elliptic elements and is analogous in its principles to Delaunay's method in lunar theory; the other is a planetary theory in which the orbital true longitude is used as independent variable; some account of this method, less well adapted for the novice, has already been published by Prof. Brown in *Monthly Notices*.

A preliminary derivation of the equations of motion is followed by a chapter devoted to theorems on formal expansions, especially in connection with Fourier series. This chapter may well be found useful for reference by many others than workers in this particular subject. The various series required in the discussion of elliptic motion are the main topic of the third chapter, and the next is occupied with the development of the disturbing function. What may be regarded as the preliminary part of the treatment is completed by a lucid introduction to the theory of canonical variables. The rest of the book deals at some length with the two principal methods referred to above, and concludes with two important chapters on resonance and on the Trojan group of asteroids respectively. Ten of these asteroids are now known, all discovered during the last thirty years; their motions

approximately realize, in association with the sun and Jupiter, the equilateral-triangle solution of the problem of three bodies whose existence was pointed out by Lagrange. The theory of these motions presents special difficulties and constitutes one of the most interesting problems with which dynamical astronomy has had to deal in recent years. The chapter on resonance includes a valuable short discussion of general principles, but naturally the authors are chiefly concerned with the examples which present themselves in the solar system. There is a short appendix on numerical harmonic analysis.

The whole book abounds in those critical and explanatory comments, on both principles and details, with which a master of his subject elucidates not only what he is doing but why he is doing it. Celestial mechanics has long been displaced from its former dominant position in mathematical curricula, but it is a pity that it is so much neglected in modern university courses; its triumphs constitute some of the most remarkable achievements of the human mind, it still presents great and fascinating problems for solution, and its study provides a valuable mathematical discipline. The student who works through these three hundred pages will certainly find his labour profitable, even if he carries his purely astronomical reading no further.

G. S. L.

Loud Speakers, Theory, Performance, Testing and Design, by N. W. McLACHLAN, D.Sc., M.I.E.E. Pp. xii + 399. (Clarendon Press, Oxford.) Price 40s. net.

This volume forms the third of the Oxford Engineering Science Series, and the author, who has made many original contributions to the subject, is a well-known authority on the design of loud-speakers. It is of interest to observe that the design of a good loud-speaker requires both scientific and engineering knowledge to no small degree—the fundamental principles of acoustics and alternating current engineering are intimately involved. It is not inappropriate therefore that this volume should be included in an "Engineering Science" series.

So much has been written about loud-speakers in a loose and popular style that it is indeed a pleasure to welcome a treatise which demands more serious consideration. A large amount of reliable scientific information has been published from time to time in this country, in America, and on the Continent, but such information has been almost obscured by the much greater volume of popular literature. British research-workers have done excellent work and Dr McLachlan himself is in the forefront. It is appropriate, therefore, that he should be the one to undertake the formidable task of collecting the scattered literature and combining it into a treatise which gives a well-balanced account of the whole subject. The author has not only done this, but has also filled in gaps by his own unpublished work.

The contents of the volume fall naturally into two parts. Chapters 1 to 12 deal with the analytical acoustical theory, i.e. the "scientific" side of the subject, whilst chapters 13 to 29 are concerned mainly with practical design and testing, i.e. the "engineering" aspect. For a thorough understanding of the theoretical section the reader will require a good mathematical knowledge, especially in regard to the use of Bessel functions; in the practical section of the book a working knowledge of the principles of alternating-current engineering is helpful, though perhaps not essential.

The theoretical section opens with a list of definitions and a brief outline of the fundamental principles relating to the radiation of sound. Following this, a number of chapters deal with the vibratory properties of diaphragms, conical shells, and rigid pistons. An important chapter relates to the spatial distribution of sound and the sound-power radiated from vibrating surfaces. Rayleigh's theory of the piston source has been extended considerably, and an original contribution by the author derives the variation of pressure over the surface of a rigid disc. The theory of moving coil and electrostatic loud-speakers is given in considerable detail, not to be found elsewhere in the general literature of the

subject. The theory of horns is treated very thoroughly, and the analytical section of the book concludes with chapters on sound waves of finite amplitude and on transients.

The technical section is concerned with the more important factors influencing the design, test, and construction of loud speakers. Driving mechanisms, magnets, efficiency, electrical impedance measurements, response curves, vibrational frequencies of conical shells, form the basis of succeeding chapters. These are followed by two important chapters on the design of hornless and of horned moving-coil loud-speakers. Numerous references to scientific literature relating to the subject are collected and conveniently arranged under subject titles, at the end of the book.

Dr McLachlan's treatise may be heartily recommended for study not only by electrical and acoustical engineers for whom it is primarily designed, but also by scientists who are more generally interested in the mathematical theory of sound and who may or may not be directly interested in the design of loud-speakers. Teachers and students will find a wealth of theoretical subject-matter of a novel kind which will repay serious study.

The book is well written in a clear style which will make a general appeal. Dr McLachlan deserves congratulation on his success in compiling such a volume, and the Oxford University Press on the selection of the author.

A. B. W.

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